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Experimental and Engineering Support for the CAFB (Chemically Active Fluid-Bed) Demonstration: Residue Disposal/Utilization

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EXPERIMENTAL AND ENGINEERING SUPPORT FOR THE CAFB DEMONSTRATION: RESIDUE DISPOSAL/UTILIZATION

C. H. Peterson, N. H. Ulerich, R. A. Newby, and D. L. Keairns

Westinghouse Research and Development Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

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EPA Project Officer: Samuel L. Rakes

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Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT The report gives results of an investigation of the disposal and utilization of spent sulfur sorbent from the Chemically Active Fluid-bed (CAFB) process. Lignite ash with a minimum of 10% CaO can be used as a replacement for sand or medium aggregate or as a partial replacement for light aggregate in cement block manufacturing with higher strengths (14.68 to 26.82 MPa) than standard mixes, 4.62 to 5.62 MPa at 28 day cure tests. This indicates that the cement content of the mix may be reduced when CAFB residue is used. Disposal tests indicate that pH, calcium, and sulfate in the leachate are primary environmental concerns. Some lignites and coal may produce levels of trace materials (e.g., selenium, iron, and manganese) that exceed regulations. Any appreciable sulfide in the spent sorbent must be converted to sulfate before disposal. Fine particle size, possibly as small as -44 μm, appears necessary for complete conversion of the calcium sulfide to calcium sulfate in completely sulfided sorbent. Cementitious compounds may be formed under CAFB operating conditions, thus aiding disposal and reducing leachates from the spent sorbent.

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ABSTRACT

This work investigated the disposal and utilization of spent sulfur sorbent from the Chemically Active Fluid-Bed (CAFB) process. Lignite ash with a minimum of 10% CaO can be used as a replacement for sand or medium aggregate or as a partial replacement for light aggregate in cement block manufacturing with higher compressive strengths, 14.68 to 26.82 MPa, than standard mixes, 4.62 to 5.62 MPa,at 28 day cure tests. This indicates that the cement content of the mix may be reduced when CAFB residue is used. Disposal tests indicate that pH, calcium, and sulfate in the leachate are primary environmental concerns. Some lignites and coal may produce levels of trace materials (e.g., selenium, iron, and manganese) that exceed regulations. Any appreciable sulfide in the spent sorbent must be converted to sulfate before disposal. Fine particle size, possibly as small as -44 μm, appears necessary for complete conversion of the calcium sulfide (CaS) to calcium sulfate ($CaSO_4$) in completely sulfided sorbent. Cementitious compounds may be formed under CAFB operating conditions, thus aiding disposal and reducing leachates from the spent sorbent.

PREFACE

The Westinghouse Research and Development Center has conducted a program under contract to the United States Environmental Protection Agency (EPA) to provide experimental and engineering support for the development of the Chemically Active Fluid-Bed (CAFB) process. The process was originally conceived at the Esso Petroleum Company, Ltd., Abingdon, UK (ERCA), as a fluidized-bed gasification process to convert heavy fuel oils to a clean, medium heating-value fuel gas for firing in a conventional boiler. Westinghouse, under contract to EPA, completed an initial evaluation of the process in 1971.[1] Conceptual designs and cost estimates were prepared for new and retrofit utility boiler applications using heavy fuel oil. Westinghouse continued the process evaluation from 1971 to 1973 and formulated an atmospheric pollution control demonstration plant program for retrofit of a utility boiler utilizing a high-sulfur, high-metals content fuel oil (for example, vacuum bottoms).[2] The CAFB process represented an attractive option for use of these low-grade fuels, for which pollution control using hydrodesulfurization or stack-gas cleaning was not economical. Application of a pressurized CAFB concept with combined-cycle power plants was also assessed.[2] Experimental support work was initiated between 1971 and 1973 to investigate two areas of concern - sorbent selection and spent sorbent processing - to achieve an acceptable material for disposal or utilization. The preliminary design and cost estimate for a 50 MWe demonstration plant at the New England Electric System (NEES) Manchester Street Station in Providence, RI, were completed in 1975.[3] Commercial plant costs were projected and development requirements were identified. Experimental support of the sulfur removal system continued in order to provide a basis for the detailed plant design. A number of design and operating parameters from the preliminary design study that

required further development were identified. The environmental impact of the disposal of unprocessed and processed spent sulfur sorbent required still further study. Between 1977 and 1981, a demonstration unit was built and operated by Foster Wheeler at the San Benito, Texas, plant of the Central Power and Light Company. This report presents the results of test programs carried out in the period 1979 to 1982 to obtain data for assessing the potential environmental impact of disposal based on materials from this unit.

Additional support work carried out under the present contract (68-02-2142) includes:

- Sorbent selection[4]
- Solids transport between adjacent CAFB fluidized beds[5]
- Sorbent disposal[6]
- Engineering evaluation of the CAFB process[7]
- Processing spent sorbent to minimize environmental impact.[8]

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NOMENCLATURE

CAFB	chemically active fluidized bed
EPA	Environmental Protection Agency
ERCA	Esso Research Centre, Abingdon, UK
EDX	energy dispersive x-ray
FBC	fluidized-bed combustion
FCC	fluid catalyst cracking
FGD	flue gas desulfurization
FOE	fuel oil equivalent
NEES	New England Electric System
NIPDWR	National Interim Primary Drinking Water Regulations
RCRA	Resource Conservation and Recovery Act
SEM	scanning electron microscopy
TDS	total dissolved solids
TG	thermogravimetry
TUGCO	Texas Utilities Gas Company
VBS	Valley Builders Supply

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We acknowledge as co-workers H. D. Smith of the Ceramics and Glasses Department, who was responsible for the disposal studies, and C. C. Sun, who was responsible for the environmental impact data. L. M. Thomas carried out the utilization tests. R. M. Martin and J. T. McAdams carried out the disposal tests. W. D. Eagleson and R. B. Stouffer made the compressive strength measurements. R. E. Brinza and J. T. McAdams carried out the environmental impact tests. C. A. Hill obtained the porosimetry results. Other Westinghouse Departments such as Analytical Chemistry and Physical Metallurgy also contributed data in this report. We also appreciate the guidance and consultation provided by D. L. Keairns, the project manager throughout these investigations.

SUMMARY

The CAFB (Chemically Active Fluidized Bed) gasification process was conceived as a means of utilizing high-sulfur residual fuel oil or refinery bottoms as fuel for conventional boilers by converting it to a low-sulfur gas. Subsequent development work and process evaluation revealed that several factors constrained its application to special situations:

- High-sulfur vacuum bottoms containing high-metal organic complexes and produced from vacuum distillation of atmospheric residual oil remain the most attractive fuels for the CAFB process.
- The availability of high-sulfur residual oil for CAFB processing is decreasing:
  - Alternative processes are available in the petroleum industry for processing high-sulfur feedstocks.
  - There is a potential demand for these feedstocks as a source of hydrogen for processing heavy crudes or alternative fuel sources such as shale oil or tar sands.
- Retrofit of the CAFB process to gas-/oil-fired boilers appears unlikely in the foreseeable future because of space requirements and the current natural gas market balance.
- The characteristics of the CAFB fuel gas (low heating value, tar content, particulate content) are not compatible with the needs of many process gas users.

A demonstration plant program sponsored by EPA was initiated with Central Power and Light in 1975 at their San Benito, Texas, plant.[9] The plant had been designed for a residual fuel oil and was adapted to investigate solid fuels, with lignite the fuel of primary interest. In view of the limited potential application with residual fuel oils, the program was also redirected to investigate solid fuels.

The objective of the present work was to investigate disposal and utilization of the spent sulfur sorbent. This was an extension of previous laboratory support work done under contract to the U. S. Environmental Protection Agency (EPA) on sulfur removal, solid transport, spent sorbent processing, and the environmental impact of residue disposal.[3-8,10]

The current work expanded the data base on CAFB residue disposal/utilization by investigations in four areas as follows:

- Utilization of regenerator residue in cement block
- Processing of regenerator residue for disposal
- Environmental impact of regenerator residues
- Processing of gasifier residue for disposal (sulfide oxidation tests).

The first, if successful, would indicate that the economics of the CAFB process might be enhanced by demonstrating that the residue had commercial value. The next two aimed at demonstrating that the residues had acceptable environmental impact, although processing them prior to disposal might be necessary. The fourth investigation aimed at making an alternative version of the CAFB process available that might be more economical because of the elimination of sulfur recovery facilities.

The San Benito unit experienced many mechanical difficulties and process upsets during the test programs. As a result of these operational difficulties, solid residues representative of steady-state CAFB process operation were not produced. Materials used in the test program included:

- Utilization tests: simulated residue using CaO and Texas lignite ash
- Disposal tests: sulfated bed material from San Benito and Esso units, San Benito boiler fines from the CAFB test, utility lignite ash, utility bituminous coal ash

- Environmental impact tests: sulfated bed material (lignite fuel); gasifier bed material, regenerator bed material, and RESOX residue (combined lignite and oil fuel test)

- Sulfide oxidation: Dolomite 1337.

The utilization tests conducted, therefore, were limited to feasibility tests: i.e., would the residues in an appropriate mix harden and develop acceptable properties? The disposal tests, on the one hand, were to show that the San Benito materials behaved environmentally like the residues from Esso Research Centre, Abingdon, UK (ERCA) and, on the other, to extend the data base on long-term stability of the residues when fixed. Finally, the tests on gasifier residue were basically feasibility tests of a modified CAFB process.

For the residue utilization tests, a simulated regenerator residue was used consisting of a lignite ash doped with calcium oxide (CaO). For the disposal tests and the environmental impact tests residues from actual operations were available. For the gasifier residue studies, Dolomite 1337 was used as the sulfur sorbent.

The important results of the laboratory-scale tests conducted may be summarized as follows:

Utilization tests

- Lignite ash to which has been added 10 wt % CaO when used as a replacement for sand or medium aggregate or as a partial replacement for light aggregate in cement block mixes resulted in higher compressive strengths.

- Use of the CaO/lignite blends may permit reduction of the cement content of the mix.

- Adequate green strength for the substituted mixes appears possible.

Disposal Tests

- Cementitious compounds may be formed under CAFB operating conditions from reactions between calcined limestone and either impurities in the limestone or constituents of fuel ash.

- Grinding CAFB residues and including sand in the mix may be necessary conditions for achieving fixation through cementitious reactions.

Environmental Impact Tests

- Leaching tests on San Benito residues, in general, gave results similar to those from previous work.

- Environmental concerns continue to be the potential levels of pH, calcium, and sulfate in leachates.

- For lignite feed, since ash compositions do vary widely, some trace elements, notably selenium, iron, and manganese, may exceed environmental regulations.

Sulfide Oxidation Tests

- Fine particle size, possibly as small as -44 μm, appears necessary for complete conversion of calcium sulfide (CaS) to calcium sulfate ($CaSO_4$) in Dolomite 1337 that is completely sulfided.

- Utilization of limestone or dolomite in desulfurization may be constrained by the ability to convert the sulfide to sulfate for disposal.

CONCLUSIONS

UTILIZATION TESTS

1. Lime/lignite fly ash mixes appear to be useful as substitutes for some of the constituents of commercial cement block mix.

2. Reduction of the cement content of the normal commercial mix may be possible through inclusion of lime/lignite fly ash mixes.

DISPOSAL TESTS

1. Grinding CAFB bed residues to at least -125 μm may be a necessary step in processing the residues to fixed masses instead of relying on the particle size reduction that occurs during slaking.

2. Limestone/conventional fly ash and limestone/fly ash mixes develop cementitious behavior after exposure to temperatures and residence times typical of the CAFB process. This behavior may also contribute to the reduced activity of the limestone as a sorbent for SO_2.

3. The results probably still cannot be considered representative of CAFB residues since the residues tested were produced under other than normal operating conditions. We believe, however, the results are at least indicative of those that would be obtained with representative materials.

ENVIRONMENTAL IMPACT TESTS

1. The environmental concerns with CAFB residues continue to be calcium, sulfate, total dissolved solids (TDS), and pH in potential leachates.

2. Trace element levels in leachates remain below 100 X those of the National Interim Primary Drinking Water Regulations (NIPDWR), and thus the leachates may be classed as nontoxic.

3. Levels for individual trace elements are subject to at least a twofold variation reflecting the ash analysis.

SULFIDE OXIDATION TESTS

A once-through limestone or dolomite process for sulfur removal is constrained by the inability to convert the CaS in the spent sorbent to the more inert form, $CaSO_4$, for disposal. Although essentially 100% calcium sulfidation can be achieved during desulfurization, complete conversion of the sulfide to sulfate is not possible for sorbent particle sizes larger than 400 μm. Two process options, however, exist. They are:

- Grind the spent bed material to very small particle sizes, possibly as small as 40 μm, and then oxidize the fine particles completely.
- Limit the utilization of calcium in the desulfurization step to a level (< 50%) that permits complete oxidation of the spent bed material.

RECOMMENDATIONS

1. Conduct further studies in the fixation of lime-based spent sorbents:*

   a. Partition the total variance in compressive strength of 5-cm test cubes among variables such as particle size, alumina content, and prior heat treatment.

   b. Study the long-term stability of fixed residues with respect to hydration of residual alkalis and sulfate resistance.

   c. Examine microscopically 5-cm test cubes at various stages of curing to identify the bond.

2. Evaluate the once-through, calcium-based sorbent concept with sulfide oxidation for disposal to determine its economic potential relative to flue gas desulfurization (FGD) and fluidized-bed combustion (FBC).

3. If the economics are favorable, develop an oxidation process for sulfided lime-based sorbents:

   a. Define process implications for a fine particle (e.g., 100 μm mean particle size) oxidizer.

   b. Identify desulfurizer design implications when used with a coarse particle (e.g., 1000 μm mean particle size) oxidizer.

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*Fixation of lime-based spent sorbents can be applied to other fossil fuel procesing technology as well as to CAFB. Thus, this recommendation does not depend on commercialization of CAFB.

1. INTRODUCTION

1.1 PREVIOUS WORK

The CAFB (Chemically Active Fluidized Bed) gasification process, in which limestone or dolomite removes the sulfur from fuel gas during gasification, was developed to permit the utilization of high-sulfur residual fuel oil or refinery bottoms in conventional boilers by producing a low-sulfur fuel gas. Coal has also been investigated as a fuel. The process can be operated as a once-through limestone sorbent system, a sorbent regeneration/sulfur recovery system, or a sorbent regeneration system without sulfur recovery by capturing sulfur dioxide (SO_2) from the regenerator off-gas with the spent stone. The spent stone from each system alternative can be processed to minimize the environmental impact of the waste stone for disposal or to provide material for potential market utilization.

Under contract to the U.S. Environmental Protection Agency (EPA), Westinghouse carried out laboratory support work on sulfur removal, solid transport, and the environmental impact of residue disposal.[3-8,10] Esso Research Centre, Abingdon, England (ERCA) carried out pilot-scale tests to investigate sulfur removal.[11] At San Benito, Texas, a 10 MW demonstration plant was retrofitted by Foster Wheeler Energy Corporation and Central Power & Light Company to permit larger-scale testing.[12]

The CAFB process produces spent sorbent, a dry limestone (or dolomite) with particles up to 6000 μm in size. The composition of the spent stone will depend on the characteristics of the original stone, the fuel fed, the process operating conditions, and the spent sorbent processing system. Spent sorbent compositions for the once-through and regenerative operating modes are shown in Table 1.

Table 1

TYPICAL CAFB SPENT SORBENT COMPOSITIONS

Component	Solids Composition, wt %: Regenerative (regenerator solids)	Solids Composition, wt %: Once-through (gasifier solids)
CaO	85-95	50-75
CaS	2-5	25-50
$CaSO_4$	2-4	~1
Inerts	1-10	1-10

Several processing alternatives have been explored that convert calcium oxide (CaO) and calcium sulfide (CaS) to an environmentally acceptable form for disposal or further utilization. Dry sulfation and dead-burning are examples of dry processing systems; slurry carbonation and wet sulfation are examples of the wet methods investigated.

Factors affecting the disposal/utilization of the spent sorbent include the quantity of spent sorbent, its chemical characteristics, environmental regulations, geographical location, and the size of markets for potential applications.

Environmentally, disposal may pollute the air with fugitive dust or with odor [e.g., hydrogen sulfide (H_2S) from hydrolysis of residual CaS]. Water pollution may result from contact with natural waters. Precipitation can generate leachates (runoff and permeate) that might pollute surface streams or groundwater. Experimental laboratory work was carried out to obtain information on the environmental impact of land disposal of unprocessed and processed spent sorbent.[6] Processing work to investigate possibilities for minimizing leachate generation and for utilizing the solid residues included other experimental work and engineering evaluations.[8]

Overall, we concluded that unprocessed CAFB residues, because of the CaO and CaS, would be environmentally unacceptable for direct land disposal, but processed residues could be so disposed of as a solid waste. Environmental concerns would be mainly about pH, calcium, sulfate ion, and total dissolved solids (TDS) in potential leachates. On the basis of environmental impact, the high-temperature processing or dry sulfation options are the recommended processes, followed by dead-burning and low-temperature fly-ash blending. There are advantages and disadvantages to each method of processing, and the decision for each application would be based on the balance of technical, environmental, and economic factors.

A comparison of the environmental impact of the disposal of unprocessed CAFB solid wastes and FGD sludge residues from varying processing systems suggested that the disposal of the CAFB solid waste might cause comparable environmental effects (due to chemical properties) but perhaps less negative (due to physical properties), than the disposal of the residue from currently commercialized flue gas desulfurization (FGD) processes.

This assessment, however, was based on results from a continuing program that was limited by the fact that spent CAFB materials were available only from a pilot-scale operation and in small quantities. These conclusions were, therefore, considered preliminary, to be reassessed as more representative samples became available from a larger-scale plant.

Development of the CAFB process achieved another milestone with the construction of the demonstration unit at San Benito. It was coupled to a Foster Wheeler RESOX sulfur recovery section operating on the regenerator off-gas. The RESOX chemistry was based on direct reduction of SO_2 with carbon from anthracite coal. This unit was expected to produce solid residues that would be representative of the CAFB process.

1.2 OBJECTIVES

The objective of the work described in this report was to expand the data base on CAFB residue disposal/utilization by investigations in four areas as follows:

- o Utilization of regenerator residue in cement block
- o Processing of regenerator residue for disposal
- o Environmental impact of regenerator residue
- o Processing of gasifier residue for disposal.

The first, if successful, would indicate that the economics of the CAFB process might be enhanced by demonstrating that the residues had commercial value. The next two aimed at demonstrating that the residues had an acceptable environmental impact, although processing them prior to disposal might be necessary. The fourth investigation aimed at making available an alternative version of the CAFB process that might be more economical because of the elimination of sulfur recovery facilities.

1.3 SCOPE

The planned scope of the work was to perform tests only on material considered representative. Unfortunately, mechanical difficulties and process upsets restricted operation of the demonstration unit to short runs. The regenerator, in particular, often was not on stream. This was a serious obstacle to the disposal work because the spent residue, basically a calcined limestone with minor amounts of $CaSO_4$, CaS, and carbon, would normally be withdrawn from the regenerator.

An alternative mode of operation was implemented in which the gasifier was run normally (reducing conditions) and then switched to oxidizing conditions to convert CaS to $CaSO_4$. The oxidized residue could then be withdrawn and discarded. This residue, however, could contain much larger amounts of $CaSO_4$ than that from the normal regenerator bed material. We believed, however, that useful information could be obtained from tests on such material.

Because of these circumstances, the utilization tests conducted were limited to feasibility tests: i.e., would the material in an appropriate mix harden and develop acceptable properties? The disposal tests, on the one hand, were to show that the San Benito materials behaved environmentally like the Abingdon residues and, on the other, to extend the data base on long-term stability of the residues when fixed. Finally, the tests on gasifier residue were basically feasibility tests of a modified CAFB process.

2. APPROACH

Investigations in four separate but related areas as noted above were planned, on the assumption that adequate test quantities of residues would be available from the San Benito demonstration unit. Three of these investigations related to the normal, regenerative CAFB process, while the fourth explored a once-through version in which the residues tested were from the gasifier bed.

The utilization tests involved measuring the compressive strength of 5-cm cubes cast from mixes based on a commercial cement block formulation in which one or more ingredients were replaced by CAFB residues. Development of strengths at least equal to those of commercially produced cement block would indicate the basic feasibility of such replacement and would thus justify the further testing outlined in Appendix A.

The processing tests (Appendix B) were initially intended to test the long-term stability of fixed CAFB residues. The residues actually tested behaved differently from previous residues; i.e., they did not display significant cementitious behavior. The program was, therefore, modified to develop an explanation for the difference. Besides studying the variations in mix composition, we made comparative studies of conventional fly ashes, including the effect of exposure to temperatures like those in the CAFB regenerator (1070°C) on cementitious behavior, and physical examinations (gradation, microscopic appearance, and surface area).

The environmental impact tests (Appendix C) involved characterization, leaching behavior, and thermal activity, using methods developed previously. Residues from normal operation of the San Benito gasifier and regenerator, the RESOX unit, and two specimens of ash from a conventional power plant burning Texas lignite were tested. Characterization included

measurement of particle size distribution, analysis by x-ray diffraction, and observations by scanning electron microscope (SEM) and energy dispersive x-ray (EDX). Leaching tests used both 72-hour intermittent shake tests and 400-hour continuous shake tests, in each case with deionized water and buffered acetic acid. Leachates were analyzed for pH, TDS, calcium, magnesium, sulfate, and sulfur, plus an extensive list of trace constituents. The results were assessed in terms of requirements of Resource Conservation and Recovery Act (RCRA) regulations.

The gasifier residue tests (Appendix D) were an exploration of a modification of the CAFB process. Instead of oxidizing the sulfided limestone in a regnerator to drive off SO_2, one might oxidize it so as to retain sulfur as $CaSO_4$. The solid product might then be discarded to the environment or possibly be utilized. Previous Westinghouse work had revealed that sulfided limestones could not be completely oxidized to sulfated limestones. The exploration, therefore, was conducted on a dolomite, using a thermogravimetric (TG) apparatus. The effects of particle size, percent sulfidation, and oxidation temperature were investigated.

3. TEST MATERIALS

The intent of all the planned studies of disposal of CAFB solid residues was to perform the tests on samples from steady-state operation. Since the pilot plant at Abingdon was shut down, the only source of such residues was the San Benito demonstration unit, which, unfortunately, experienced many interruptions in operation. Normally, the major solid residue would be spent regenerator material; minor streams would be boiler fines and baghouse fines.

Because the regenerator, in particular, was often down, a common mode of operation was to run the gasifier normally for a time and then switch it to operate as an oxidizer. The purpose was to convert CaS to $CaSO_4$ so that the spent sorbent could be discarded in a landfill. As time passed, it became evident that if we were to obtain useful information on the disposal and environmental impact of CAFB residues, we would have to resort to using modified test materials.

The CAFB process was originally designed to gasify residual oil. The residue would normally contain about 91 wt% CaO, 3.0 wt% CaS, and 2.5 wt% $CaSO_4$, the balance being miscellaneous inert oxides.[3] Eventually the San Benito operation shifted to the use of Texas lignite, so the combined residues would then contain all the coal ash as well. Typical analyses of Texas lignite and Brownwood limestone are in Tables A-1, -2, and -3 in Appendix A, from which we estimated the composition of the residues for the gasifier/oxidizer moder of operation. We used a Ca/S molar treat ratio of 1.1:1, a lignite sulfur of 0.82 wt%, an ash of 18.39 wt%, and minimum sulfur capture of 77.4 % (equivalent to a maximum allowable emission of 260 ng SO_2/J fired). The residual composition obtained was 9.4 wt% CaO, 13.0 wt% $CaSO_4$, and 77.6 wt% inerts (mixed oxides from coal ash and limestone impurities). A further assumption was complete calcination of carbonates to oxides.

For normal operation including the regenerator, the combined residues would contain mainly coal ash and CaO. Ignoring the small to trace amounts of CaS and $CaSO_4$, the residues would have about 16 wt% CaO for the same treat ratio as above (1.1:1). We chose to simulate the residues to be used in the utilization tests by adding CaO to lignite ash from a Texas Utilities Gas Company (TUGCO) plant to the level of 10 wt% of the blend. (The TUGCO and the San Benito lignites had come from the same mine.)

Other test materials needed for Phase I were obtained from Valley Builders Supply (VBS), including light aggregate, medium aggregate, and sand.

For the disposal tests, residues were obtained from the last run at San Benito, which was Run 11, performed June 22 and 23, 1981. Start-up began at 1038 hours on the 22nd and coal feed at 1433 hours, with oil feed continued at various times. Coal feed ceased at 0315 hours on the 23rd and sulfation began. Total duration of coal gasification was 12 hours 42 minutes, of which 9 hours and 11 minutes were solely on coal at 7000 to 7600 lb/hr feed rate.

The coal was a 2.02 % sulfur West Virginia bituminous, analyses for which are in Appendix B, Tables B-10 and B-11. The sorbent was Brownwood limestone, an analysis of which is in Appendix A. Samples of gasifier bed materials were taken at 2200 hours on June 22 and after sulfation on June 23.

4. DISCUSSION OF RESULTS

4.1 UTILIZATION TESTS

Details of the utilization tests and their results are in Appendix A. Basic feasibility was demonstrated for the use of CaO-doped lignite ash as a replacement for sand or medium aggregate or as a partial replacement for light aggregate. This means, at this stage, only that (1) the mixes hardened and (2) the compressive strength developed was adequate. Further tests are still required.

As to the other VBS constraints (Table A-1), we believe the water content of the mixes can be reduced to meet the green strength requirement. The lignite ash did not meet the density criterion [1314 kg/m^3 vs 865 (82 lb/ft^3 vs 54) desired]. Alkaline fugitive dust from the CAFB residues might create personnel problems, but these probably can be avoided by handling the residues in a closed system to the point of blending with the other constituents. Since the compressive strength developed was higher than that of the controls, reduction of cement content may be possible. No data were obtained on the compatibility of the mixes with materials of construction in the existing cement block plant or on bleeding of off colors in use. No problems, however, are expected with materials of construction. If lignite ash is used, there may be some staining due to its iron oxide (Fe_2O_3) content. The typical ash, though, shows only 3.8 wt% Fe_2O_3 versus values up to 44 wt% for some bituminous coal ashes, 19 wt% for subbituminous ashes, and 18 wt% for other lignites.[13]

4.2 DISPOSAL TESTS

Details of these tests on the San Benito residues are in Appendix B. They cover two main lines of investigation: preliminary

testing at ambient temperature for cementitious behavior and testing at high temperature for possible formation of pozzolanic substances in the residues.

The first step in the planned work was to confirm by the usual 5-cm cube tests that the San Benito residues did indeed have pozzolanic activity and were therefore suitable materials for the long-term stability tests. Because the utilization tests in Appendix A had shown Texas lignite ash could be used in cement block mixes, we used boiler fines as the silica source, in the expectation that this material would contain a large fraction of the ash from the coal fed. This also was an attempt to eliminate some intermediate testing, since residue disposal from the CAFB process would have to include disposal of boiler fines. The initial mixes, however, failed to harden. We searched for an explanation of this behavior, considering the following variables: slaking procedure, mix composition, fly ash source, particle size, sulfate content, alumina content, and temperature history of the CAFB residues.

What had been demonstrated previously[8] was that regenerator bed residue from the Abingdon CAFB Run 9 in the following mixes would show cementitious behavior:

Residue + Portland cement + sand

Residue + Portland cement + sand + conventional fly ash

Residue + conventional fly ash

Ground residue + conventional fly ash.

Compressive strengths at 28 days were in the range of 1.4 to 12.1 MPa (210 to 1750 psi). We had also noted that the CAFB residues had to be slaked prior to casting to prevent expansive crumbling during subsequent curing.

The current residues exhibited a delayed slaking, i.e., they apparently did not react with water initially but developed an exothermic reaction some time after an induction period of as much as

20 minutes. Despite modifications to the slaking procedure, the specimens still failed to harden. We explored other possibilities as described in Appendix B: excessive lime in the boiler fines, insufficient active silica content in the coal ash, comparison with Abingdon gasifier residue, addition of sulfate ion via gypsum, addition of cement, and addition of alumina. No hardening comparable to previous results was obtained. The residues, incidentally, were not ground to check the effect of particle size because on slaking the residues disintegrated spontaneously.

These results could be explained by hypothesizing that either something was missing from the mixes or that something was present that inhibited hardening. The former possibility appeared to fit the observations better so we began to consider the effects of high temperature on the residues. The CAFB gasifier is intended to operate at about 870°C, the regenerator at 1070°C. The regenerator was infrequently run at San Benito, and, in fact, was not run during collection of the current test materials. Since Portland cement manufacture involves heating a finely ground $CaO/SiO_2/Al_2O_3$ mixture to sintering temperatures of 1300 to 1500°C, perhaps in the CAFB process over many cycles (since the temperature is lower) some conversion to calcium silicates, aluminates, or possible aluminoferrites may occur. This may also contribute to inactivation of the lime as a sulfur sorbent. On the other hand, operation of the gasifier as an oxidizer could have resulted in hot spots which might have produced a relatively inactive lime.

For reference, the average residence times of sorbent in the CAFB process were approximated from a design prepared for the New England Electric System (NEES).[3] These are in Table 2.

Thus, in terms of the net throughput, the sorbent makeup may remain in the gasifier typically for at least 72 hours at 870°C and in the regenerator for 5 hours at 1070°C. There are, of course, distributions of residence times about these typical values.

Table 2

ESTIMATE OF SOLIDS RESIDENCE TIME IN A CAFB PLANT[a]

	Gasifier	Regenerator
Bed Size - D x H, m (ft)	4.8 & 5.9 x 1.2 (15'10" & 19'4" x 4')	1.4 x 1.2 (4'6" x 4')
Bed Volume, dm^3 (ft^3)	27,598 (974.5)	1801 (63.6)
Solids Flow Rate		
Throughput, kg/s (lb/hr)	0.16 (1318.7)[b]	0.12 (986.1)
Total out, kg/s (lb/hr)	9.3 (73819.2)	9.1 (72600.9)
Solids Residue Time, hr		
Throughput	59.1	5.2
Total flow	1.06	0.070

[a]Plant data reported in English units.

[b]Calcined sorbent.

For the San Benito operation, the gasifier bed area was 14 m^2 (150 ft^2), and the slumped bulk density was typically 961 kg/m^3 (60 lb/ft^3). For Run 11, the operators calculated the bed height from pressure drop measurements as about 1.02 m (40 in), corresponding to an inventory of 13,608 kg (30,000 lb). Sorbent feed rate was about 0.06 kg/s (500 lb/hr). Residence time for calcined sorbent was, therefore, of the order of 110 hours. Because of carry-over, the residence time for the portion remaining in the bed would normally have been greater but, in effect, was limited by the run length to no more than 16 hours in gasification plus about 45 minutes in sulfation.

The research questions were:

1. Do cementitious compounds form in the CAFB process under the typical conditions of time and temperature?
2. Are any other variables, such as particle size, involved in the development of pozzolanic activity?

To investigate these questions, we first heat treated mixes of -1/4" Grove limestone and Ohio Edison fly ash at 1070°C for three durations: 7, 19, and 51 hours. Although some sintering occurred, specimens cast from blends of these materials with additional quantities of fly ash showed only slight hardening. Grinding the limestone to -200 mesh and heating 30 minutes at 1400°C did result in sintering. Heat treating at 1375°C for 2.5 hours yielded a granular material, the -100 mesh fraction of which hardened somewhat when water was added. In further tests, summarized in Table B-16, heating a mix of -149 μm Grove limestone with either Ohio Edison fly ash for 2.5 hours at 1375°C or with feldspar for 60 hours at 1070°C resulted in castings with compressive strengths of 4.6 to 6.6 MPa (670 to 960 psi). We consider this as evidence that cementitious compounds can form under CAFB process conditions.

The final set of tests reported in Table B-17 was performed to check differences in the pozzolanic activity of the fly ashes by a standard ASTM test. The range of compressive strengths obtained was 0.8 to 4.6 MPa (110 to 660 psi), which was less than the ASTM C 595 compressive strength requirement of 5.5 MPa (800 psi) for pozzolans for blended hydraulic cements. The Ft. Martin fly ash was not as good a pozzolan as the Keystone or TUGCO fly ashes, which were about equal (3.7 Pa vs 4.10 and 4.24 MPa respectively). The Ohio Edison was tested at a lower fly ash/lime ratio (1:1) but developed less strength than the comparable Ft. Martin mix (1.46 vs 2.01 MPa). Increasing the fly ash/lime or fly ash/residue ratio from 1:1 to 2:1 resulted in higher strengths (1.8 x for lime, 3.5 x for San Benito, and 4.1 x for ERCA). Grinding the CAFB gasifier bed residue also increased strength, but data were obtained only for the San Benito residues.

Two sets of results in Table B-17, however, support an alternative explanation for the test results. In one, TUGCO ash blended with -149 μm San Benito residue in the 2:1 ratio not only hardened, but showed a relatively high strength: 3.7 MPa (535 psi). In contrast, the same mix ratio did not harden in the test reported in Table B-3. In the

other, boiler fines with -149 μm residue in the 2:1 ratio yielded 4.4 MPa (640 psi). This also conflicts with the previous results (Table B-1 and 2). Differences in both cases were grinding the residue and including sand in the mix. Further tests are needed to separate from each other the effects of grinding the gasifier bed residues, sulfation, and the possible presence of cementitious compounds formed in the CAFB process. The presence of sand may also be a factor since bricks have been made since 1898 by autoclaving compressed sand/lime mixes in steam at pressures to 4.05 MPa (40 atm).[14] Lime content in these mixes may vary from 5 to over 50 percent (silica lime ratio of 19:1 to 1:1), depending on the strength needed. When we reviewed our previous work, we noted that in every reported test for both CAFB residues and fluidized-bed combustion residues, the residues were first ground to at least -125 μm. According to Taylor, the bond in the calcium silicate bricks is due to various hydrated calcium silicates, the nature of which depends on the Ca/Si ratio. Hence, whether or not calcium silicate-type cementitious compounds are formed in the CAFB process, on hydration these could hydrolyze to permit the usual silicate gel processes to occur. Grinding the residues may therefore be a key step in processing the CAFB residues to fixed masses. The essential constituents of the mix thus appear to be finely divided silica (probably less than 145 μm) plus active CaO or $Ca(OH)_2$. The role of cementitious compounds formed at high temperature could be to increase the compressive strength of the fixed residues from, say, less than 3.45 MPa (500 psi) to over 6.9 MPa (1000 psi).

4.3 ENVIRONMENTAL IMPACT TESTS

Details of these tests and their results are in Appendix C. In general, the tests on the San Benito residues gave results similar to those from previous work on CAFB residues. As in the case of work reported in the other appendices, there is some continuing uncertainty arising from the lack of truly representative residue test materials. Individual lots of coal also vary in their trace element content. In

the present samples, for instance, substances exceeding drinking water regulations for leachates from the regeneration residue were Ca, Se, and SO_4. Some elements may exceed the regulations - Fe, Mn - whereas in tests on regenerator residue from the lignite run at ERCA (CAFB-11), these elements (Fe, Mn, Se) were within regulatory limits.

Overall, we should expect that proper design of the disposal facility would minimize leachate formation, so that trace elements would not be an environmental concern. High pH and TDS due to Ca and SO_4 remain as the particular concerns.

4.4 SULFIDE OXIDATION TESTS

Details of these tests and their results are in Appendix D. While 100 percent sulfidization of Dolomite 1337 was achieved for five particle size fractions over the range of 44 to 1680 μm, 100 percent sulfation was demonstrated only for the 44 to 53 μm particles. This was done at the low end of the temperature range used (600°C).

For completely sulfided 710 to 840 μm particles, increasing temperature from 500 to 900°C resulted in increasing sulfation from 4 to 58%. Data scatter obscures a possible peak conversion greater than 58% at 800°C.

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APPENDIX A

UTILIZATION TESTS

PHASE I - FEASIBILITY TESTS

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APPENDIX A

UTILIZATION TESTS

PHASE I - FEASIBILITY TESTS

INTRODUCTION

An alternative to mere disposal of solid residues from the CAFB process is utilization, which could enhance the economics of the process. An opportunity to explore this potential was found through a San Benito cement block manufacturer, Valley Builders Supply (VBS). A test program was devised to determine whether spent regeneration bed material could replace one or more of the components of the VBS block mix.

There were several constraints on materials substitution, as noted in Table A-1.

The general objectives of the proposed tests were as follows:

- Evaluate the potential for utilizing solid residues produced during operation of the CAFB process with residual oil and with lignite fuels in building block.
- Evaluate the environmental impact of processed solid residues using tests developed at Westinghouse under contract to EPA and EPA tests proposed under the Resource Conservation Recovery Act (RCRA)
- Perform systems evaluation to assess the effect of process operation on residue disposal/utilization.

WORK PLAN

Delays in performance of these tests resulted when actual residues were not available from operations in oil feed and when operating difficulties with lignite feed were experienced. It was

Table A-1

CONSTRAINTS ON USE OF CAFB SPENT STONE IN CEMENT BLOCK

1. Minimum cement content
2. Maximum bulk density of aggregate to be 865 kg/m^3 (54 lb/ft^3)
3. Minimum compressive strength of block produced of 7.58 MPa (1100 psi) on any face
4. Adequate green strength
5. No bleeding of off colors in use
6. Compatibility of mix with existing materials of construction in the block plant.
7. No new personnel problems

---

finally agreed to proceed with Phase I of the test program covering feasibility tests using a simulated residue. The work plan was updated to show a program consisting of five phases.

Phase I - Feasibility Tests. Bench-scale feasibility tests using lignite ash and simulated spent sorbent to confirm that, when these materials are used to replace one or more components of the current VBS mix, the modified mixes will harden to solid blocks. Similar tests were previously carried out using ERCA pilot plant residues for residual oil operation.

Phase II - Product Characteristics. Bench-scale tests with actual residues from the demonstration plant using lignite and residual oil fuels to establish product characteristics such as long-term stability and potential environmental impact.

Phase III - Demonstration Tests. Demonstration tests at VBS to confirm full-scale operability on mixes using actual residues. Characteristics of the product blocks would be compared with laboratory tests. Environmental impact tests would be performed.

Phase IV - Production Runs. Based on successful demonstration tests and a selection of mix composition, production runs would be carried out at VBS to confirm recommendations and performance estimates.

Phase V - System Evaluation. System evaluation to integrate findings on residue characteristics, processing options, and estimated environmental impact would be carried out.

Only Phase I was carried out, since samples representative of the normal CAFB operation were never produced. Tests in Phase I include exploration of mix composition, physical inspections, and chemical analysis.

MIX COMPOSITION

Objectives

Two different objectives applied. For lignite operation, the quantity of solids produced by the CAFB plant was large enough for us to consider using it to replace sand, fine aggregate, medium aggregate, limestone dust, or a combination of these. For oil operation, the question was rather one of the feasibility of disposing of solids by incorporating them into cement block. A secondary objective was to determine whether any improvement in quality resulted, permitting reduction of Portland cement. In both cases, a further objective was to determine whether any deleterious effects result. In either case, compositions would be considered satisfactory if compressive strengths in excess of 1100 psi were obtained.

Feasibility tests were made with 5-cm cubes. Maximum replacement of solids in the existing mix formulas was set at 20 percent, based on matching production rates of the San Benito and the VBS plants. Four sets of tests in duplicate were planned, each including three different simulated spent sorbents as noted in the main text. Controls using the current VBS formulation were included. Quality was judged by the compressive strength developed at 3, 7, 28, and 90 days.

Compositions

Compositions selected for the strength tests are in Table A-2. The composition labelled LC was the current mix. In L1, sand was omitted completely and replaced by the simulated residue. In the remainder of the test mixes, the simulated residue content was set at 20 wt% and the amounts of the other components reduced as shown. Thus, the medium aggregate was omitted completely in Mix L3, while the limestone dust was omitted completely in Mix L4. Light aggregate was effectively reduced 46 percent in Mix L2 and 29 percent in Mix L4.

Compressive Strength

Test specimens were 5-cm cubes cast in triplicate from the above mixes and tested for compressive strength in accord with ASTM C 109 at four moist-curing times: 3, 7, 28, and 90 days. Data are in Table A-3 and plotted on Figure A-1.

Table A-2

COMPOSITION OF TEST MIXES

	Composition, g				
	L1	L2	L3	L4	LC
Light Aggregate	434	234	434	306	434
Medium Aggregate	200	200	-	200	200
Limestone Dust	72	72	72	-	72
Sand	-	180	180	180	180
Portland Cement	114	114	114	114	114
CAFB Sorbent and Ash Residue	180	200	200	200	-
	1000	1000	1000	1000	1000

Table A-3

COMPRESSIVE STRENGTH OF 5-cm CUBES CAST FROM MIXES CONTAINING SIMULATED CAFB LIGNITE RESIDUE, MPa[a]

Mix	Curing Time, days			
	3	7	28	90
L1	6.03	8.48	25.10	34.68
	10.45	12.41	28.59	31.03
Average	8.24	10.44	26.82	32.86
Range, ± %	27	19	6	6
L2	6.41	9.52	22.41	28.27
	8.41	12.96	19.72	42.06
Average	7.41	11.24	21.06	35.16
Range, ± %	13	15	6	20
L3	7.79	11.58	22.68	19.30
	8.62	11.44	22.48	25.51
Average	8.20	11.51	22.58	22.40
Range, ± %	5	0.6	0.4	14
L4	8.48	10.62	15.31	28.96
	8.76	8.48	14.06	27.23
Average	8.62	9.55	14.68	28.10
Range, ± %	2	11	4	3
LC1	3.79	5.86[b]	5.31	16.27
	3.72	5.03[b]	5.93	17.58
Average	3.75	5.45[b]	5.62	16.92
Range, ± %	1	8	6	4
LC2	3.45	-	5.03	6.96
	3.52	-	4.20	5.31
Average	3.48	-	4.62	6.13
Range, ± %	1	-	9	14

[a]MPa = 145.038 psi.

[b]9-day values.

One set of cement mortar control specimens failed to develop normal strength (14 to 42 MPa). The 90-day point for the second control series (LC2) was much lower than that for LC1 (6.1 vs 16.9 MPa), attributable to the fact that the mixes were tamped in the mold rather than vibrated as were all other specimens. The effect may have been due to a lower rejection of excess water. Whatever the reason, both sets of control specimens developed lower compressive strengths than any of the test mixes.

As a check on the compressive strength criterion, two 3.8-cm cubes were cut from pieces of cinder block manufactured by VBS. Compressive strengths were 13.8 and 10.6 MPa (2000 and 1540 psi). These values are at the low end of the range for normal concrete (14-42 MPa). Building brick is in the range of 10 to 21 MPa (1500-3000 psi). Previous work with 5.08-cm cubes of various size fractions of CAFB regenerator stone and coal fly ash had yielded compressive strengths in the range of 0.9 to 2.2 MPa (125-313 psi) after 21 days of curing and 1.3 to 2.8 MPa (193-405 psi) after 66 days of curing. These compositions, however, did not contain Portland cement as did the cinder block specimens. We concluded that this level of pozzolanic activity indicated potential for utilization of CAFB residues.

Most of the 23 pairs of results were within 10 percent of the mean strength for the pair. Three pairs had a spread of ± 15 percent, two had 20 percent, and one (L1, 3 days) had ± 27 percent. All four test mixes showed compressive strengths in excess of that desired (1100 psi or 7.58 MPa), even at 7 days. All had the same cement content (114 g/1000 g dry mix). The fact that L3 had the lowest 90-day strength of the four test mixes may suggest that lignite ash is not a substitute for medium aggregate, but L2 results show that lignite doped with 10 percent CaO might replace 46 percent of the light aggregate. Mixes L1 and L2 are preferred on the basis of their early development of high strength. L1 is preferred over L2 in eliminating one ingredient, sand.

All of the mixes appear superior to the commercial mix, even at 3 days. All develop strength much like normal concrete, rapidly to 28 days and then at a slower increase to ultimate strength. The commercial mix develops only about half the 7-day strength of the test mixes and then remains essentially constant to about 28 days. The strength may then increase to about 15 MPa.

These data suggest that CaO-doped lignite ash may not only be a substitute for a part of one or more ingredients of the commercial mix, but may also impart superior strength to the product. The amount of lime used in these mixes corresponds to a 1:1 molar treat ratio for a wet lignite containing 18.4 percent ash and 0.82 percent sulfur. This is equivalent to 0.104 g CaO/g ash.

Figure A-2 shows cubes cast from the various mixes and moist cured for 90 days. Figure A-3 shows the failure mode in compression for cubes cured for 28 days.

PHYSICAL INSPECTIONS

Unit Weight

Data on the unit weight of 5-cm cubes cast from the various test mixes are given in Table A-4. The specimens used had been moist cured for 90 days. The volume of each specimen was determined in two ways: by water displacement and by calipering. Because the surfaces of the specimens were irregular, the calipering method overstates their volume, especially in the case of control specimens. The unit weights obtained by water displacement for blocks made from the test mixes were within the range bracketed by the control cubes.

Table A-5 presents data on the unit weight of dry mixes. These were obtained by measuring the volume occupied by a weighed amount of mix in a graduated cylinder. "Loose" density is for the unconsolidated mix, "tamped" is after consolidation by tapping the cylinder on a hard surface until constant mix volume has been obtained. The control mix unit weight is equivalent to 1206 kg/m^3 (75.3 lb/ft^3), whereas the lignite ash is 1307.2 kg/m^3 (81.6 lb/ft^3). One of the desired criteria

Table A-4

UNIT WEIGHT OF 5-cm TEST CUBES PREPARED FROM SIMULATED CAFB RESIDUE

		Cube Volume		Unit Weight, g/ml	
Specimen	Cube Weight, g	By Water Displacement, ml	By Calipering, cm^3 (in^3)	By Water Displacement, ml	By Calipering, cm^3 (in^3)
L190	229.3	130	136.3 (8.315)	1.764	27.57 (1.682)
L290	247.5	130	134.5 (8.209)	1.904	30.16 (1.840)
L390	246.6	125	136.0 (8.299)	1.973	29.72 (1.813)
L490	234.8	125	134.8 (8.225)	1.878	28.55 (1.742)
LC190	194.2	100	132.2 (8.068)	1.942	24.08 (1.469)
LC290	193.7	110	131.7 (8.036)	1.761	24.11 (1.471)

Table A-5

UNIT WEIGHT OF TEST MIXES

		Volume		Unit Weight, g/ml	
Specimen	Wt, g	Loose, ml	Tamped, ml	Loose	Tamped
LC1	112.2	100	93	1.122	1.206
Lignite Ash	115.1	100	88	1.151	1.308

was that the aggregate unit weight should be no more than 865 kg/m^3 (54 lb/ft^3). As produced, the lignite ash is not a candidate for lightweight block.

Green Strength

In a commercial block plant, the molds are removed within minutes after casting, so the mix consistency must be such that the demolded blocks retain their shape. The consistency is probably dependent mainly on the water content needed for plasticity, since the time involved is too short for cementitious reactions to proceed very far. Valley Builders Supply referred to the consistency characteristic as "green strength." It may be tested as per ASTM C 143. The 30.48 cm (12 in) cone in this test, however, requires 5.7 dm^3 (0.2 ft^3) of mix per test. Instead, a 15.24 cm (6 in) cone was used, Figure A-4, reducing the mix requirement to 0.02 dm^3 (0.025 ft^3) per test. A correlation to convert the slump obtained with the 15.24 cm (6 in) cone to an equivalent slump for a 30.48 cm (12 in) cone based on work by Smith et al.[A1] is:

$$S_L = 0.236 + 2.135\ S_s$$

where S_L = slump in a large [30.48 cm (12-in)] cone
and S_s = slump in a small [15.24 cm (6-in)] cone.

Slump data on selected mixes are in Table A-6

Table A-6
SLUMP DATA FOR SELECTED TEST MIXES

	Slump, in		
Mix. No.	Observed in 15.24 cm (6-in) Cone	Estimated for 30.48 cm (12-in) Cone	Water Content of Mix, wt %
LC	0.64 (0.25)	1.96 (0.77)	12.0
L3	2.54 (1.0)	6.1 (2.4)	14.0
L4	3.18 (1.25)	7.37 (2.9)	14.0

Since block mixes are usually of a no-slump consistency, the slumps for mixes L3 and L4 are probably too large. Reduction of the water content should reduce slump, but further tests were deferred.

Chemical Analyses

Typical chemical analyses of Texas lignite, Texas lignite ash, and Brownwood limestone are in Tables A-7, -8 and -9.

Table A-7

TYPICAL CHEMICAL ANALYSIS OF TEXAS LIGNITE, SULPHUR SPRING, TEXAS[a]

	As Received	Dry
Proximate Analysis, wt%		
Fixed Carbon	23.80	34.10
Volatile Matter	27.59	39.55
Ash	18.39	26.35
Moisture	30.22	-
	100.00	100.00
Ultimate Analysis, wt%		
C	35.75	51.23
H	4.50	6.45
N	0.24	0.35
S	0.82	1.18
O	10.08	14.44
Ash	18.39	26.35
Moisture	30.22	-
	100.00	100.00
High Heating Value, J/g (Btu/lb)	14235 (6122)	20306 (8733)
Air dry loss, wt%	21.62	

[a]From Foster Wheeler Fuel Analysis Report, 10/24/78.

Table A-8

TYPICAL CHEMICAL ANALYSIS OF TEXAS LIGNITE ASH

	Wt. %	g Moles/100 g Ash
SiO_2	54.5	0.9070
Al_2O_3	22.0	0.2158
Fe_2O_3	3.8	0.0238
CaO	8.0	0.1426
TiO_2	1.4	0.0175
MgO	1.4	0.0347
Na_2O	0.5	0.0081
K_2O	0.9	0.0096
SO_3	5.6	0.0700
P_2O_5	0.1	0.0007
Undetermined	1.8	-
	100.0	

[a]From Foster Wheeler Fuel Analysis Report 10/24/78.

Table A-9

CHEMICAL ANALYSIS OF BROWNWOOD LIMESTONE

	Wt%	Normalized Wt%	g Moles/100 g
CaO	53.3	52.57	0.9374
MgO	0.53	0.523	0.0130
CO_2	43.6	43.00	0.9770
Al_2O_3	0.94	0.93	0.0091
Fe_2O_3	0.97	0.96	0.0060
SiO_2	1.84	1.82	0.0303
Na_2O	0.026	0.0258	0.00042
K_2O	0.17	0.168	0.00178
Cl	0.0032	0.0032	0.000090
	101.3792	100.0000	

REFERENCES

A-1. Smith, L. M. et al, Technology for Using Sulfate Waste in Road Construction, Gilette Research Institute, Rockville, MD, Report to Federal Highway Administration, FHWA-RD-76-31, December 1975.

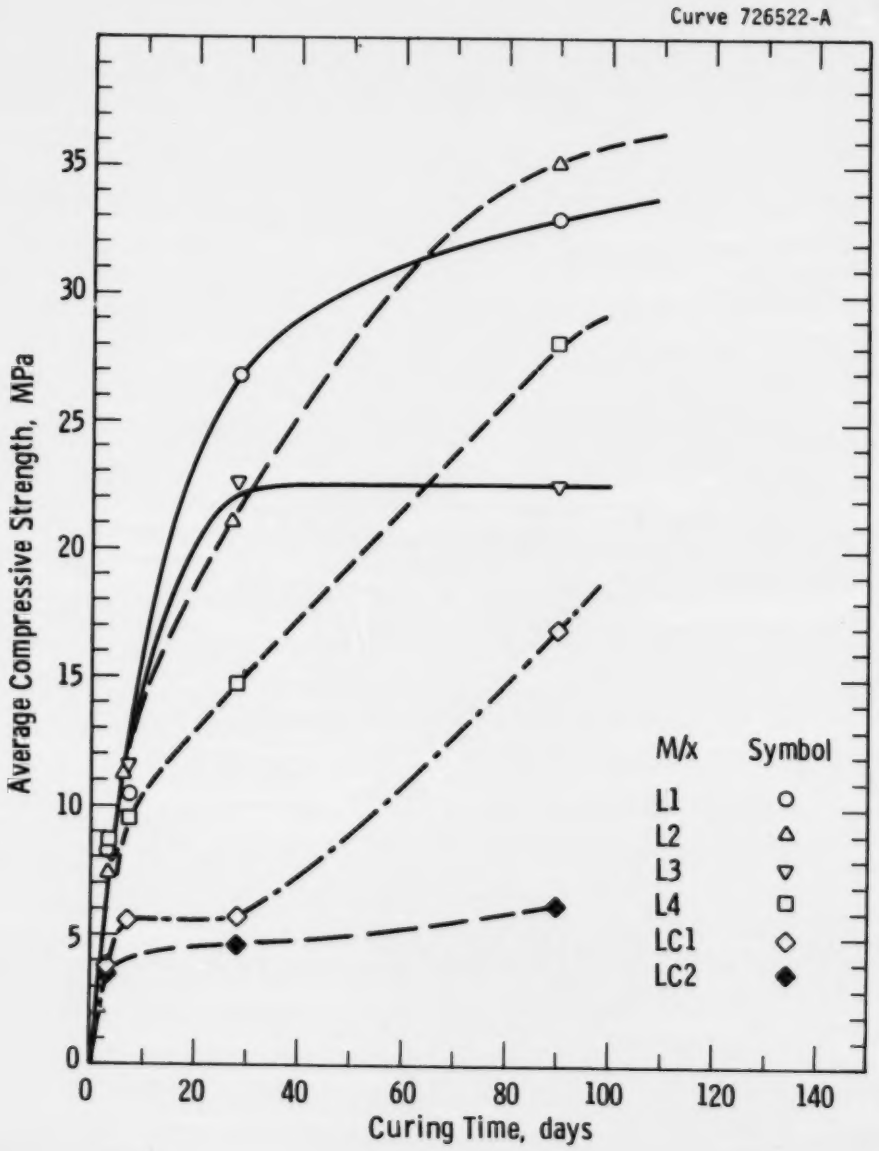


Figure A-1 - Compressive Strength of 5-cm Cubes Cast from Lignite Ash Mixes.

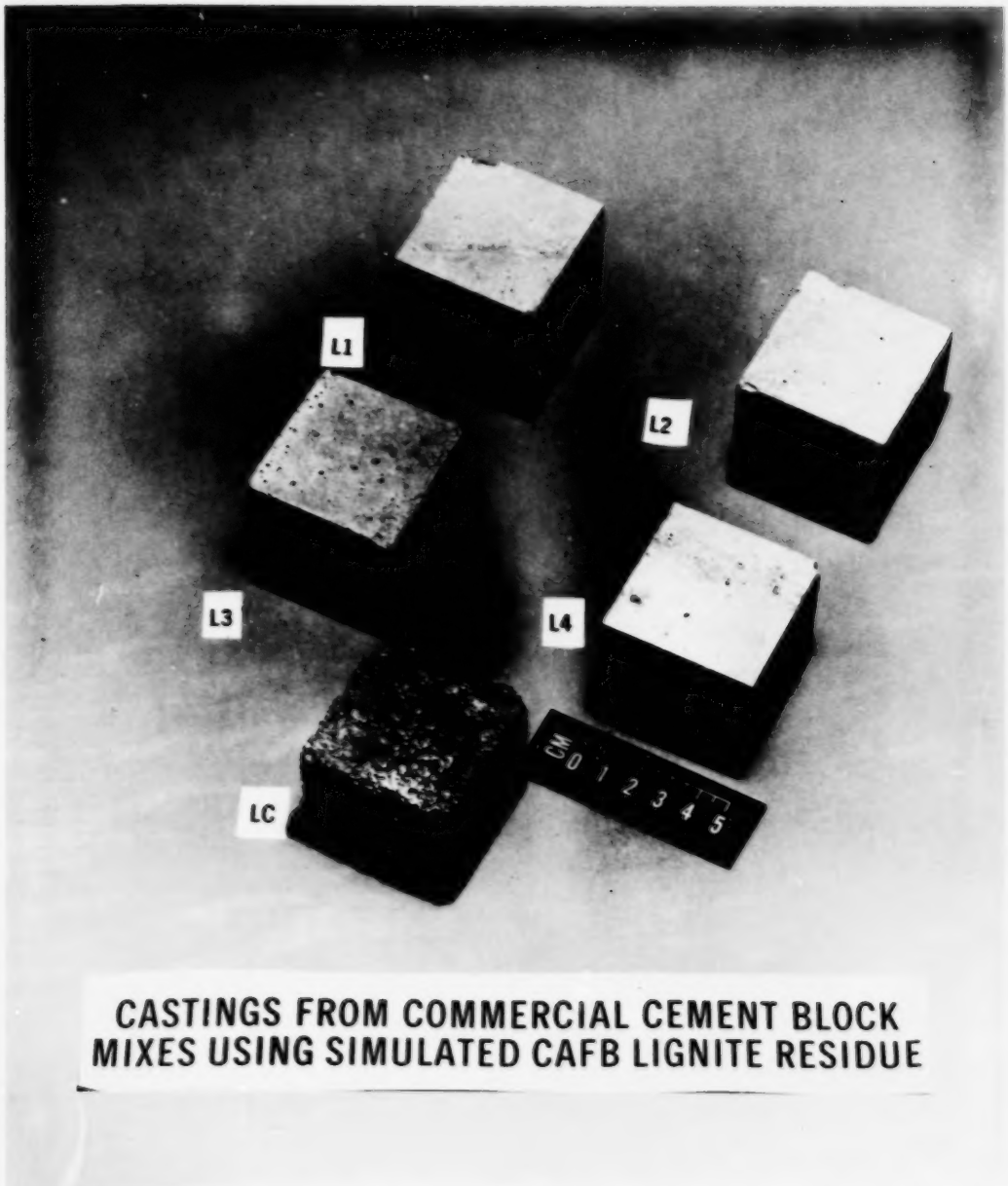


Figure A-2 - Cubes Cast from the Various Mixes and Moist Cured for 90 Days

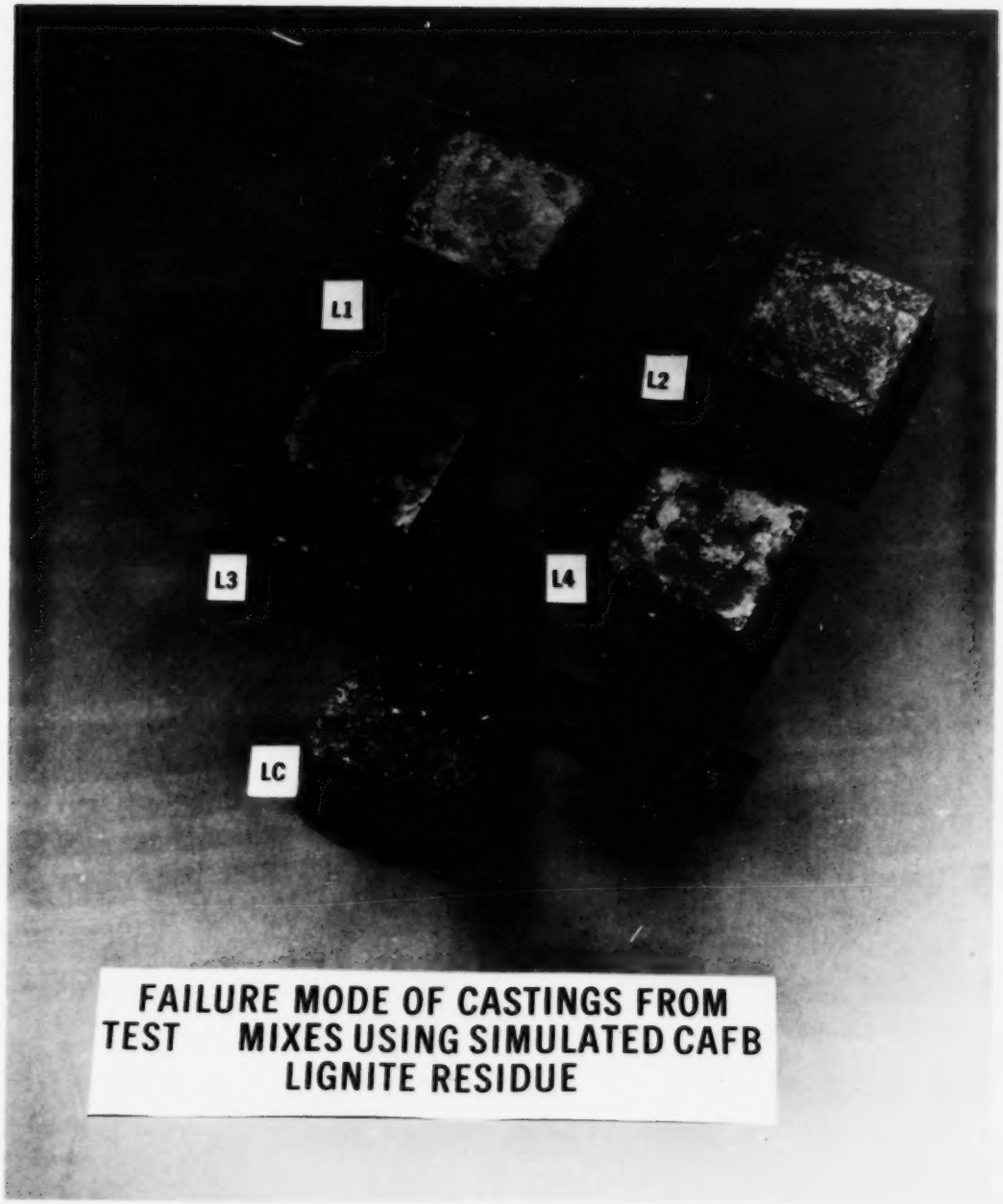
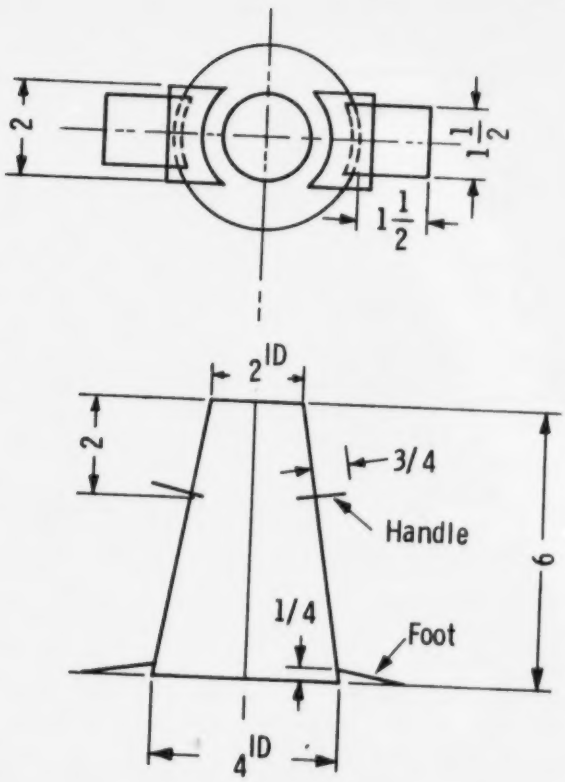


Figure A-3 - Failure Mode for Cubes Cured for 28 Days

Dwg. 7726A12



Material: 304 SS, Minimum Thickness 16 BWG

Notes – 1. All Joinings Are Welded
2. Inside Surface of Cone to Be Smooth
3. All Dimensions are in Inches. Tolerance on Overall Dimensions ± 1/16"
4. Attach Handles Perpendicular to Lateral Surface of Cone
5. Seam on Cone to Be Butt Joint

Figure A-4 - Slump Cone

APPENDIX B

DISPOSAL TESTS WITH CAFB RESIDUES

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APPENDIX B
DISPOSAL TESTS WITH CAFB RESIDUES

PRELIMINARY TESTS

As a preliminary to testing the long-term stability of fixed residues, initial laboratory tests were conducted, pending receipt of chemical analyses to confirm that the current specimens of residues from the San Benito test unit could be fixed as shown by previous work.

The tests involved blending spent bed material that was known to be high in calcium oxide (CaO) with a siliceous material, such as fly ash. With the addition of water to form a paste and moist curing for 24 hours, such mixtures have usually hardened at least enough to permit handling. Test 1 used sulfated bed material and boiler fines from the San Benito unit, shown in Table B-1. The boiler fines are a mixture of fines deposited in the boiler from several runs. It should contain ash from the lignite burned as well as spent sorbent fines.

Table B-1

TEST 1: BLENDS OF SULFATED BED MATERIAL WITH BOILER FINES

	SSG-1	SSG-2	SSG-3
Sulfated bed material, g	30	10	10
Boiler fines, g	30	30	50
Deionized water, ml	240	160	240

In each case the ingredients were combined in Nalgene beakers to permit slaking of the free CaO, and excess liquid was decanted. Each dish was placed in a plastic bag. After the dish had been covered with a wet paper towel, the bag was wired closed and allowed to stand overnight. Results were as follows:

SSG-1 Material had tripled in volume but was not coherent.

SSG-2 Material had expanded in volume and showed cracks in one area.

SSG-3 Material did not expand but had developed cracks.

When water was added, the slaking reaction took 15 minutes for SSG-3, about 25 minutes for SSG-2, and even longer for SSG-3. The excess water was decanted after a short stirring time.

When these specimens failed to harden, the slaking procedure was modified for Test 2. It has been shown previously that material incompletely slaked before casting would expand later as the slaking continued and crack the castings. A further possibility was that the particles in the current test material were coated in some manner that rendered them inactive.

To rule out the possibility that slaking was incomplete in the previous test, the procedure was modified by using 240 ml deionized water for each mix and letting the slurries stand for 1 hour, with occasional manual stirring. Test mixes and results were as in Table B-2.

Table B-2

TEST 2: MODIFIED SLAKING PROCEDURE

	SSG-1R	SSG-2R	SSG-3R	SSG-4R
Sulfated bed material, g	30	15	10	60
Boiler fines, g	30	45	50	0
Temperature, ^{o}C	29	26	25	35
pH	12.08	11.95	11.90	11.85

Each sample was then filtered through a Millipore 0.45 μm filter. The solids were returned to their respective Nalgene beakers, and water was added to achieve the consistency of wet concrete. The beakers were covered with wet paper towels and allowed to stand

overnight in sealed plastic bags. Again, no perceptible set in the material developed in 24 hours.

Test 3 substituted Texas Utilities Gas Company (TUGCO) fly ash, a lignite ash, for the boiler fines on the possibility that the boiler fines contained excessive amounts of lime from sorbent carry-over. Less water was added and temperature rises were recorded. Mix compositions and temperature data are in Table B-3.

Table B-3

TEST 3: BLENDS OF SULFATED BED MATERIAL WITH TUGCO FLY ASH

	SSG-5	SSG-6	SSG-7	SSG-8
Sulfated bed material, g	40	40	30	20
TUGCO fly ash, g	10	20	30	40
Water, ml	100	120	120	120
Temperature, ^{o}C				
15 mins	42.0	38.0	34.0	30.0
30 mins	44.0	41.0	36.5	31.5
60 mins	35.5	34.5	32.5	28.5

The lime in the San Benito gasifier bed material, while active, appears to be relatively dead-burned. For specimen SSG-5 a peak temperature rise of about $24^{o}C$ was noted over a period of 30 minutes. Neglecting heat losses, about 11,305 J (2700 cal) were released rather than the potential 50,663 (12,100). More precise measurements may be made later, if needed.

After 24 hours of curing in sealed plastic bags, SSG-5 and SSG-8 seemed to show some hardening, but the other two specimens remained like mud. After 48 hours of further curing, we concluded that none of the specimens had hardened.

Test 4 substituted Duquesne fly ash, a bituminous ash, for the TUGCO ash for its higher silica content, but still no hardening occurred after 24 hours of curing in sealed plastic bags. Data are in Table B-4.

Table B-4

TEST 4: BLENDS OF SULFATED BED MATERIAL WITH DUQUESNE FLY ASH

	SSG-9	SSG-10	SSG-11	SSG-12
Sulfated bed material, g	40	40	30	20
Duquesne fly ash, g	10	20	30	40
Water, ml	100	120	120	120
Temperature, °C				
15 min	38.0	35.0	32.0	30.0
30 min	40.5	38.0	34.0	31.0
45 min	41.0	39.0	35.0	<31.0
60 min	38.5	36.0	33.0	29.5

In Test 5 the slaking procedure was modified to minimize the amount of water added so that no constituents would be lost when excess water was discarded from the slurries.

Water was added in stages as the blends became either dry, hot, or both over a 42-minute period. The mixes were then placed in plastic weighing boats that had been sprayed with Teflon mold release. These were covered with damp paper towels, sealed in plastic bags, and cured for 24 hours. Similar mixes were prepared using TUGCO fly ash.

Similar mixes were also prepared using spent gasifier bed material from Run 12, Esso Research Centre, Abingdon, UK (ERCA). Mix data are in Tables B-5A, B, and C respectively.

After 24 hours of curing, specimens SSG-9 through 12 were dry, cracked, and had no perceptible hardening. Specimens SSG-5R through 8R behaved similarly. All the specimens made from ERCA residue (EG-1 through 4) remained as mud. The specimens were cured further for a total of 33 days. The physical condition of the specimens is in Table B-6. Both sets of blends with Duquesne showed weak bonding at the lowest levels of fly ash (4 bed material:1 fly ash). This was a qualitative judgment based on the coherence exhibited when the sample

Table B-5

TEST 5: MODIFIED SLAKING PROCEDURE

5A. Duquesne Fly Ash/San Benito Residue Mixes

	SSG-9R	SSG-10R	SSG-11R	SSG-12R
Sulfated bed material, g	40	40	30	20
Duquesne fly Ash, g	10	20	30	40
Water, ml				
Initial	50	40	20	20
Total	54	48	33	23

5B. TUGCO Fly Ash/San Benito Residue Mixes

	SSG-5R	SSG-6R	SSG-7R	SSG-8R
Sulfated bed material, g	40	40	30	20
TUGCO fly ash, g	10	20	30	40
Water, ml				
Initial	50	40	20	20
Total	53	48	32	20

5C. Duquesne Fly Ash/ERCA Residue Mixes

	EG-1	EG-2	EG-3	EG-4
Gasifier bed material, g	40	40	30	20
Duquesne fly ash, g	10	20	30	40
Water, ml				
Initial	75	50	30	25
Total	75	70	50	32

was subjected to bending. With the TUGCO fly ash, some bonding occurred at higher levels of fly ash (< 1 bed material:1 fly ash). The "bonding" in all cases was weak.

A few additional tests were made for mixes to which gypsum, aluminum oxide, or sand were added. None of these hardened. Overall, these results supported the view that some high-temperature processing was needed to develop cementitious behavior.

Table B-6

PHYSICAL CONDITION OF SPECIMENS FROM TEST 5
AFTER 33 DAYS OF MOIST CURING

Specimen Number	Bed Material Source	Fly Ash	Physical Condition
SSG-9R	San Benito Gasifier	Duquesne	Weak bonding
10R			Trace bonding
11R			Crumbly
12R			Crumbly
SSG-5R	San Benito Gasifier	TUGCO	No bonding
6R			No bonding
7R			Weak bonding
8R			Weaker bonding
EG-1	Esso England Gasifier	Duquesne	Trace bonding
2			Trace bonding
3			Crumbly
4			Crumbly

CHARACTERIZATION OF TEST MATERIALS

Gradation

Gradations for the bed materials are given in Table B-7. The San Benito material is basically -4750 +500 μm, while the Abingdon material is -4750 +250 μm. Gradation of the Ohio Edison fly ash was determined by screening a 200 g sample on a Ro-Tap machine for 90 minutes. Results are in Table B-8.

Chemical Analysis

Chemical analyses for the residues are in Table B-9. The San Benito material is a high-lime residue with a lime:silica weight ratio of about 20 as compared to the English medium-lime residue with lime:silica at about 3. The finding of major significance is the low sulfur levels. Either sulfur was not absorbed during gasification or it was largely driven off as SO_2 during sulfation.

Tables B-10 and 11 give analyses for the coal fed and its ash. Table B-12 shows an analysis of Ohio Edison ash, while Table B-8 shows a typical TUGCO ash.

Microscopic Examination

Since we believe the cementitious reactions involved in the tests of spent bed residues to be largely surface reactions, we examined selected test materials under microscopes.

Figures B-1A and 1B show 200X and 800X optical microscopic views of an oil suspension of the Ohio Edison fly ash. Four basic particle types are visible:

Amorphous, dark	Soot
Angular, transparent	Mineral fragments
Transparent, varicolored spheres	Glass and agglomerates
Composites	Agglomerates of the above

Table B-7

GRADATION OF CAFB RESIDUES

Sample Source	Wt% Oversize		
	San Benito		Abingdon
Sample	Gasifier Bed Material	Sulfated Bed Material	Gasifier Bed Material
Screen Opening, µm			
4750	0.10	0.15	1.29
2000	19.15	20.66	6.69
1000	76.67	76.48	45.78
500	99.67	99.39	91.81
250	99.92	99.92	99.29
75	99.97	99.97	99.90
0	100.00	100.00	100.00
Loss, g	0.1	0.4	0.8
Original Sample, g	1000.0	1000.0	1010.0

Note: Gradations were obtained by sieving on Ro-tap machine for 10 minutes.

Table B-8

GRADATION OF OHIO EDISON FLY ASH

U.S. Sieve Size	Wt% Retained	Cumulative Wt% Retained	Appearance
+100	0	0	--
-100 +140	13.9	13.9	Black particles
-140 +170	5.1	19.0	Mainly black particles
-170 +200	3.3	22.3	Fewer black particles
-200 +240	3.8	26.1	Predominantly light gray
-240 +270	21.4	47.5	Light gray
-270	52.5	100.0	Light gray

Table B-9

CHEMICAL COMPOSITION OF CAFB RESIDUE MATERIALS, wt%

Sample Source	San Benito		Abingdon
Chemical Constituent	Sulfated Bed Material	Gasifier Bed Material	Gasifier Bed Material, Run 12
CaO	88.15	90.67	64.36
MgO	1.13	1.56	1.41
SiO_2	4.53	4.19	23.98
Al_2O_3	1.46	1.12	6.64
Fe_2O_3	2.06	2.02	1.84
$SO_3^=$	0.85	0.20	0.57
$S^=$	0.03	0.22	0.01
C	0.11	0.37	0.91
	98.32	100.35	99.72
Undetermined	1.68	(0.35)	0.28
LOI	0.81	0.07	2.04

Table B-10

TYPICAL ANALYSIS OF WEST VIRGINIA BITUMINOUS COAL[a]

	As Received
Proximate Analysis, wt%	
Fixed carbon	52.34
Volatile matter	35.70
Ash	7.83
Moisture	4.13
	100.00
Ultimate Analysis, wt%	
C	75.15
H	4.82
N	1.12
S	2.02
O	4.93
Ash	7.83
Moisture	4.13
	100.00
High Heating Value	
J/g (Btu/lb)	31170 (13407)

[a]Per Foster Wheeler telephone communication, August 10, 1981.

Table B-11

TYPICAL ANALYSIS OF WEST VIRGINIA BITUMINOUS COAL ASH

	Wt% [a]	g Moles/100 g Ash
SiO_2	45.5	0.7572
Al_2O_3	28.3	0.2776
Fe_2O_3	13.0	0.0814
CaO	3.6	0.0642
TiO_2	1.3	0.0163
MgO	1.1	0.0273
Na_2O	<0.1	<0.0016
K_2O	1.5	0.0159
SO_3	3.5	0.0437
P_2O_5	0.2	0.0014
Undetermined	1.9	
	100.0	

[a]Per Foster Wheeler Telephone communication, August 10, 1981.

Table B-12

CHEMICAL ANALYSIS OF OHIO EDISON FLY ASH

	Wt% [a]	g Moles/100 g Ash
SiO_2	48.56	0.8081
Al_2O_3	22.77	0.2233
Fe_2O_3	4.99	0.0312
CaO	2.25	0.0401
TiO_2	1.15	0.0144
MgO	0.45	0.0112
Na_2O	0.24	0.0039
K_2O	2.18	0.0269
SO_3	0.64	0.0080
P_2O_5	0.12	0.0008
Total C	13.95	1.1614
Undetermined	2.70	-
	100.00	
LOI	15.68	

[a]Average of two determinations by Westinghouse Analytical Chemistry Department.

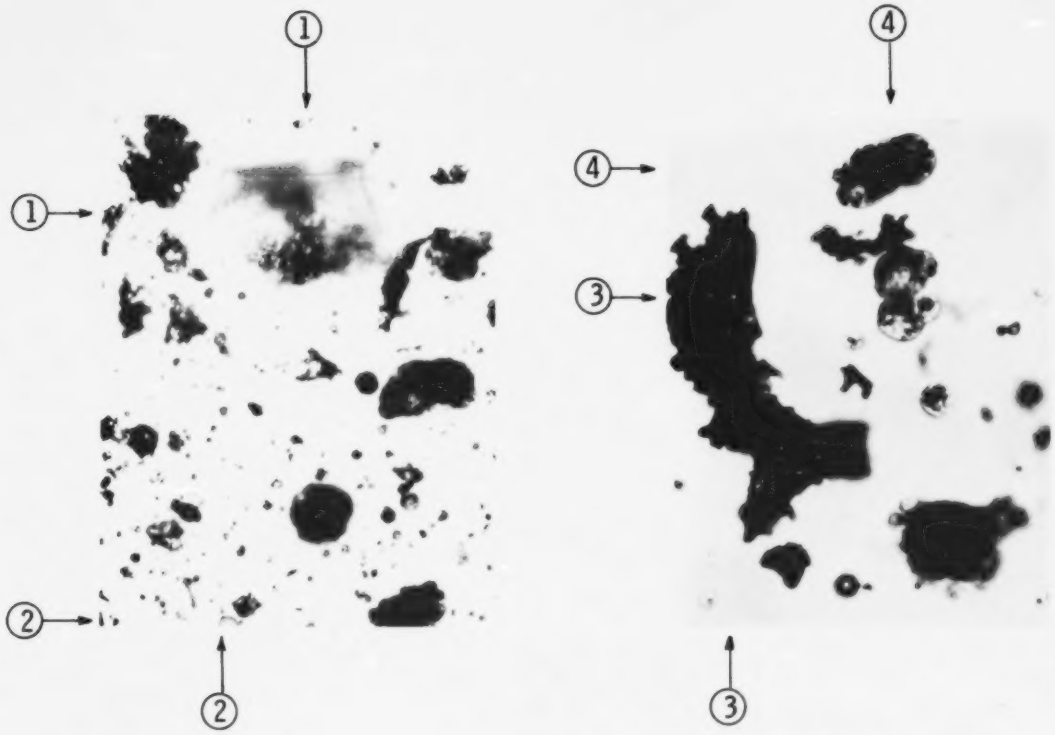


Figure B-1 -- Oil Suspension of Ohio Edison Fly Ash under Optical Microscope

1	-	1	Mineral Fragment	3	-	3	Soot Particle
2	-	2	Glass Sphere	4	-	4	Agglomerated Spheres

We are tentatively considering the black particles to be soot and the gray material to be noncarbonaceous glass droplets and mineral fragments.

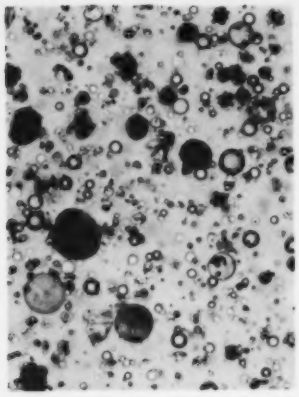
Three other fly ashes were also examined microscopically: TUGCO fly ash, Pennsylvania Electric fly ash (Keystone plant), and boiler fines from the San Benito test unit. They were examined in a standard index oil (n = 1.5150 at 23°C) with the optical microscope. Both TUGCO and Keystone fly ashes contained the characteristic fly ash components: glass spheres, mineral fragments, agglomerates of glass and mineral (crystalline) materials, and carbon (coke particles) with mineral fragments. In contrast, the San Benito boiler fines contained little recognizable fly ash material and a few corroded spheres. Most of this material appears to be fine, irregular, crystalline grains, as shown in the photographs (see Figure B-2).

These ashes, in contrast with the Ohio-Edison material, do not have a great deal of carbonaceous matter and seem to have a proportionally greater amount of glass as spheres and odd-shaped agglomerates.

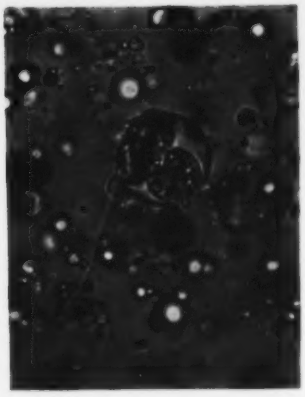
Keystone and TUGCO ashes both contain plerospheres, cenospheres, partially devitrified spheres, and spheres of different colors. The two ashes appear to differ in two ways: the Keystone contains more coke particles than the TUGCO and a greater variety of glass colors. Otherwise, they look the same. Duquesne and Ft. Martin materials look much like the Keystone fly ash.

Grains of CAFB residues from San Benito and Abingdon were mounted on an aluminum stage using silver paint. This process was carried out in a dry, N_2-filled glove box to eliminate contamination with atmospheric moisture. The mount was coated with gold and loaded into the scanning electron microscope (SEM). Figures B-3, 4, and 5 show 50X and 10,000X views of these materials.

At 10,000X (actual magnification is indicated by the bar, at the right edge of the picture, which represents 5 μm), the Abingdon and the San Benito materials consist of a large percentage of submicron

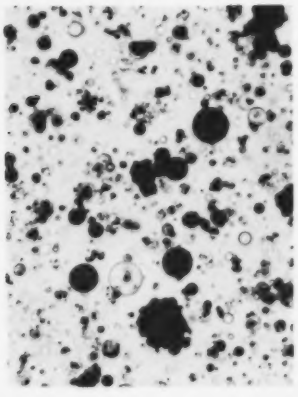


320X



800X

A. TUGCO Fly Ash



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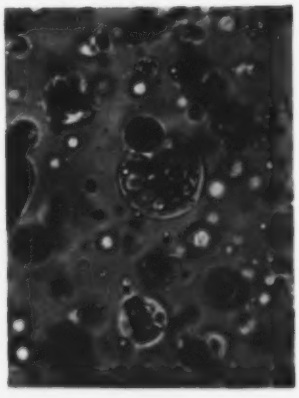
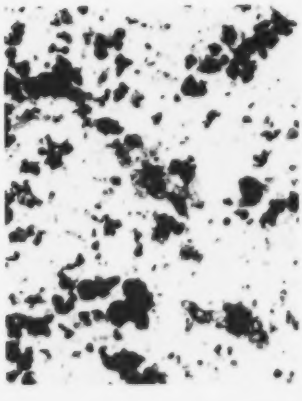


800X

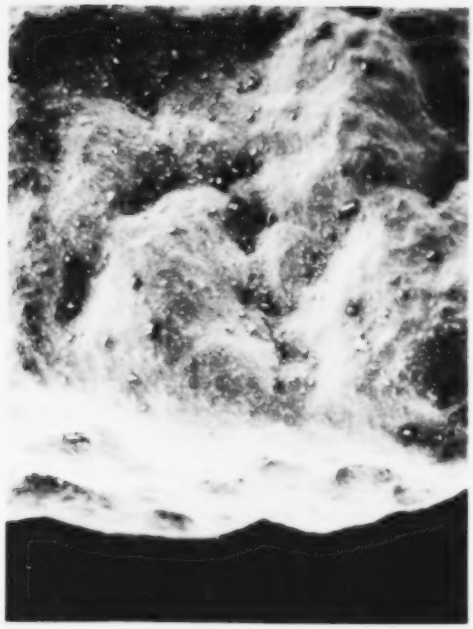
B. Keystone Fly Ash



126X

C. San Benito Boiler Fines

Figure B-2 -- Optical Microscopic Views of Selected Fly Ashes



A. Magnification 50X

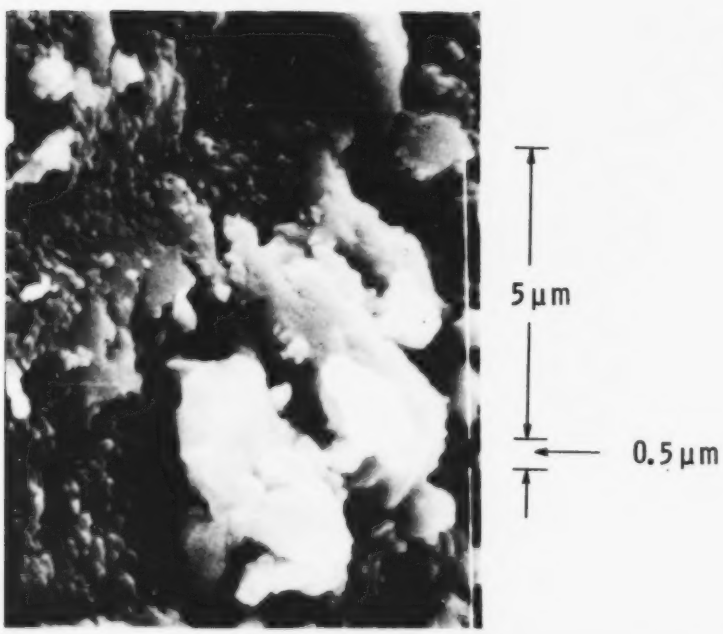
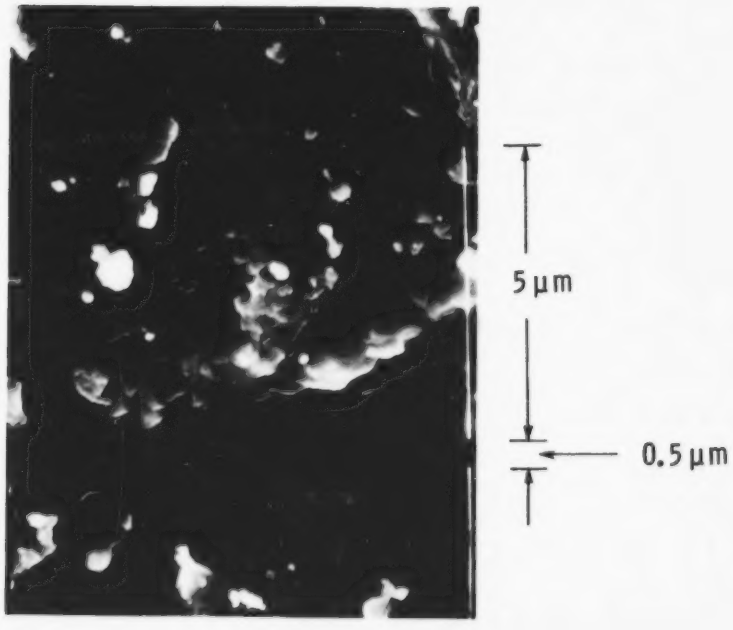


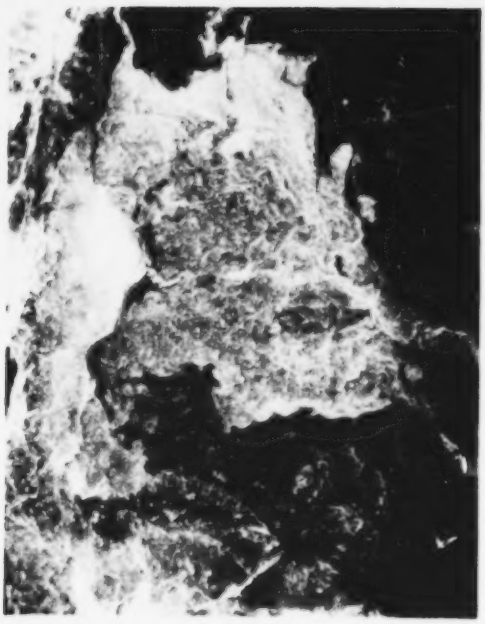
Figure B-3 -- Spent Gasifier Bed Material from CAFB Unit, San Benito, Texas

A. Magnification 50X

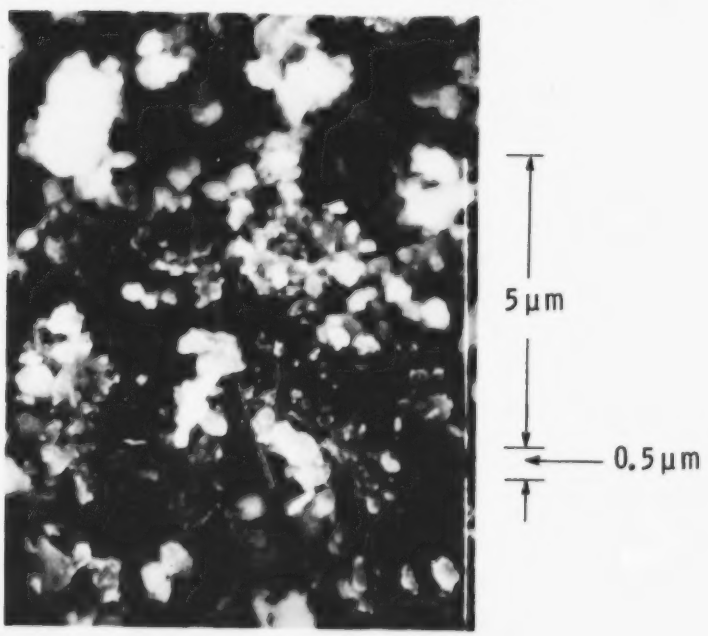


B. Magnification 10000X

Figure B-4 -- SEM Views of Oxidized Spent Gasifier Bed Material from CAFB Unit, San Benito, Texas



A. Magnification 10000X



B. Magnification 10000X

Figure B-5 -- Spent Gasifier Bed Material from CAFB Unit, Abingdon, England

particles, and the sulfated San Benito has a distinctly coarse and more regular texture. The fine texture and open-pore structure at the surface is consistent with the vigorous slaking action observed when water is added to these materials. They also break up into a very fine-grained material while slaking.

Mercury Porosimetry

Table B-13 shows characterization data on four fly ashes by mercury porosimetry. All three fly ashes that had shown good pozzolanic activity had large surface areas: 12.9 to 19.5 m^2/g. In contrast, the low activity Ohio Edison ash had a surface area of only 0.5 m^2/g. It appears this ash has nearly 40 percent of its pore volume in pores with diameters larger than 10.5 μm versus 8 to 21 percent for the other three ashes. Much of this may, however, be interparticle voids. Less than 0.5 percent of its pores are in sizes smaller than 2.1 μm versus about 9 percent for the other ashes. The three active fly ashes also show similar distributions of pore volumes by pore diameters for diameters less than 4.1 μm

HIGH TEMPERATURE TESTS

Fly Ash/Limestone Blends

Batches of -1/4 in. Grove limestone (378 g) and as-is Ohio Edison fly ash (422 g) were mixed in a V-blender for about 20 minutes. Each batch was then calcined in a ceramic crucible in an electric furnace at 1070°C using three different calcination times, as shown in Table B-14. All of the mixes sintered to a soft, friable, bricklike material, shrinking away from the crucible wall in the process.

The average weight loss was 228 g, of which perhaps 166 g was due to loss of carbon dioxide from the limestone. The rest (62 g) is equivalent to 14.7 percent loss if attributed to the fly ash. Measured LOI for the fly ash was 15.7 ± 0.8 percent.

Figures B-6 and B-7 show the appearance of the mix of Ohio Edison fly ash and -1/4 in. Grove limestone that had been heat treated at

Table B-13

CHARACTERIZATION OF FLY ASHES BY MERCURY POROSIMETRY

Company	Duquesne Light Company	Monongahela Power Company	Ohio Edison	Pennsylvania Electric Company
Plant	-	Ft. Martin	-	Keystone
Total intrusion volume, cc/g	0.3824	0.4252	0.5422	0.3971
Total pore area, m^2/g	15.9327	19.4885	0.4785	12.8649
Median pore diameter, μm				
By volume	4.1822	3.6980	4.8779	3.5732
By area	0.0042	0.0044	3.1660	0.0051
Average pore diameter, μm	0.0960	0.0873	4.2329	0.1235
Bulk density, g/cc	1.1484	1.1404	0.6826	1.1589
Apparent (Skeletal) density, g/cc	2.0476	2.2137	1.0836	2.1470
Distribution of pore volume, wt%				
+ 10.5 μm	13.5	8.2	29.1	21.0
- 10.5 + 7.5	3.9	0.0	3.1	0.7
- 7.5 + 5.4	25.7	5.2	9.7	12.7
- 5.4 + 4.1	16.7	38.0	14.9	14.6
- 4.1 + 3.3	8.7	10.6	13.0	10.2
- 3.3 + 2.1	11.3	14.8	19.8	15.6
- 2.1 + 1.3	11.4	13.9	2.1	17.0
- 1.3 + 0.1	2.1	2.0	0.2	2.1
- 0.1	6.7	7.3	0.1	6.1

Table B-14

CHARACTERISTICS OF GROVE LIMESTONE/OHIO EDISON FLY ASH BLENDS

	Batch Number					
	90-1	91-4	90-2	91-2	91-1	91-3
Calcination time, hr	--- 51-------		---- 19 ---		--- 7 ---	
Weight, g						
Initial	800	800	800	800	800	800
Final	570	568.6	581	568.8	572.6	572.4
Color						
Initial	Dark gray		Dark gray		Dark gray	
Final	Dull brown-red		Dull brown-red		Dull brown-red /dark gray	

1070°C for 19 hours. The fly ash appears to have sintered lightly, possibly incorporating some of the limestone fines. The large particles of limestone appear only to have been calcined.

As an exploration of the loss in weight and the color changes, two batches were heated, one in air, the other under a stream of about 5 ℓ/min of nitrogen directed over the top of the charge. The former was red-brown throughout, while the latter had a light red-brown band only at the top. We conclude that air oxidation occurred when the batches were heated in air but have deferred more definitive tests of this behavior.

The two batches for each temperature were mixed together after the + 0.64 cm (1/4 in) particles were removed by screening and then stored in plastic bags under dry nitrogen. Each mix was then divided into three equal aliquots of about 380 g each and Ohio Edison fly ash added in the amounts, 0, 10, and 20 wt% of the final blends. Water was added to slake the free lime present. All the batches became very hot. Excess water was decanted, and the pastes were allowed to cool. The pastes were then packed into cylindrical molds 2.22 cm D x 3.81 cm H (7/8 in. D x 1-1/2 in. H), and set aside to cure at 100 percent relative humidity for 7, 28, and 51 days. A total of 81 specimens were prepared: 3 calcining times x 3 fly ash contents x 3 curing times x 3 replicates.

A

Heated in air

B

Heated with nitrogen flush

Figure B-6 -- Ohio Edison Fly Ash/Grove Limestone Sinter as Removed from Crucible

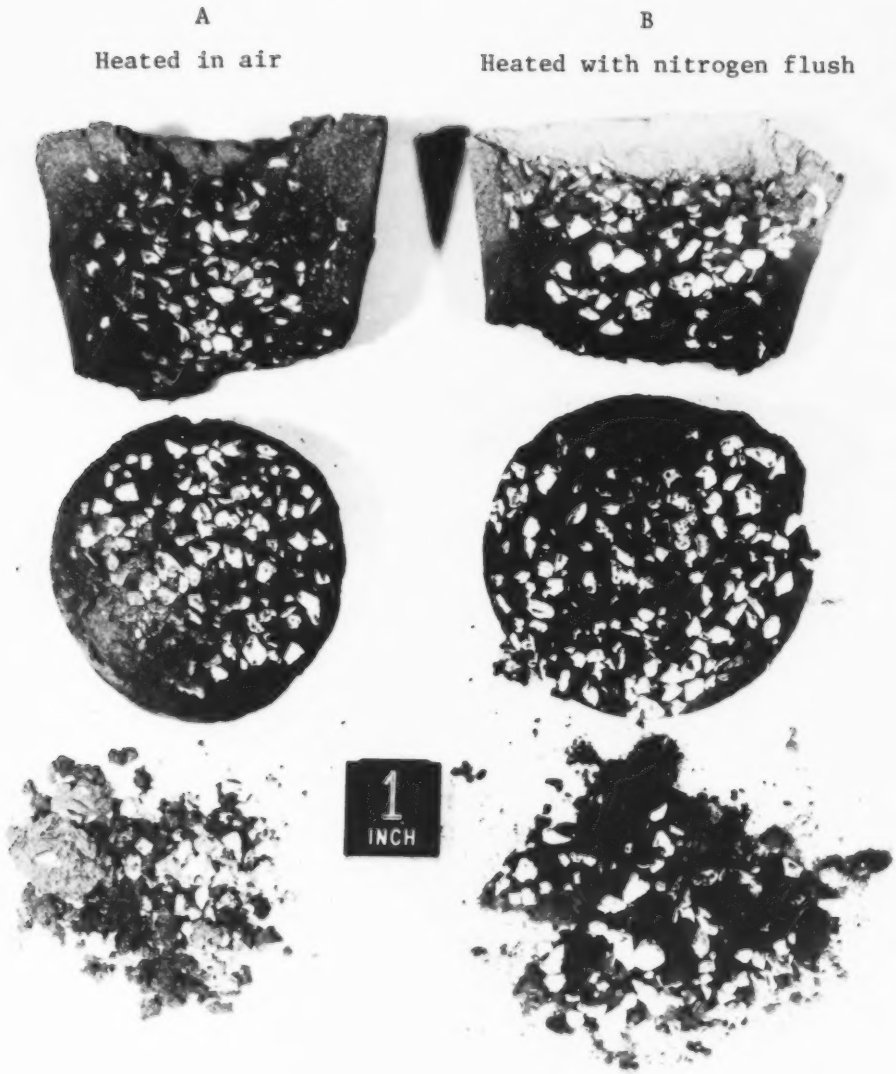


Figure B-7 -- Ohio Edison Fly Ash/Grove Limestone Sinter after Sectioning

1 Diametral vertical section of crown
2 Plan view of midsection
3 Unconsolidated material from bottom section

Only a little cementlike hardening of the specimens occurred. At seven days, all samples could be crushed between thumb and forefinger. Some samples, particularly those containing no additional fly ash, were barely able to retain their shape after removal from the molds. After 28 days, the samples were generally firmer but still very weak. The specimens that contained 20 percent fly ash plus material calcined for 7 hours could not be crushed between thumb and forefinger. Hardness increased in all samples on curing in air but was still much less than that of concrete.

Figure B-8 shows test specimens made from the heat-treated mixes. They have continued to harden, if we may judge by observations made after 50 days' curing under 100 percent humidity at room temperature. In general, increased fly ash content relative to the heat-treated fly ash/limestone primary mix results in increased hardness. Increased heat-treating time appears to inactivate the mix. Whether the limestone, the fly ash, or both are inactivated is unclear.

This experiment suggests that Ohio Edison fly ash does have some pozzolanic activity. As applied to the CAFB process, it supports the earlier finding that the San Benito residues did not set up when blended with various fly ashes. It does not agree, however, with previous tests on residues from Abingdon on oil gasification residue.

Since the heating at 1070°C did not conclusively demonstrate the formation of cementitious substances, Grove limestone was ground to 100 percent through a No. 200 U.S. sieve and blended with Ohio Edison fly ash in a weight ratio of 1.79:1. This was estimated to correspond to a $CaO:SiO_2$ mole ratio of 2:1. Cylindrical pellets 6.4 mm D x 6.4 mm H (1/4 in. D x 1/4 in. H) were pressed and heated in air in a muffle furnace at various temperatures for 30 minutes. At 1400°C the pellets fused to a hard clinker, but at 1375°C only a friable compact formed. The effect of time and temperature was explored further by heating batches of the above mix at 1375°C for 2.5 hr, 1200°C for 18 hr, and 1070°C for 125 hr. All remained granular.

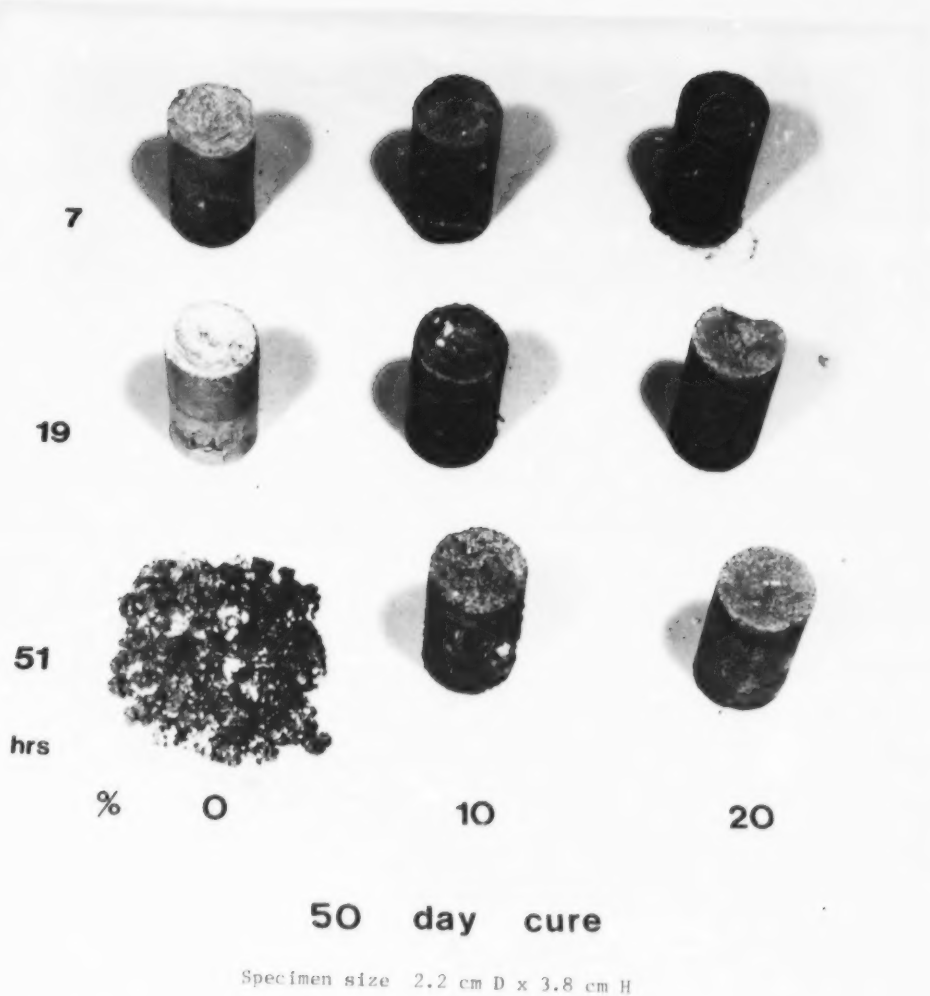


Figure B-8 -- Pozzolanic Activity of Heat-Treated Ohio Edison Fly Ash/Grove Limestone Blends

Forty gram portions were passed through a No. 100 sieve, combined with water, cast in 2.22 cm D x 3.81 cm H (7/8 in. D x 1-1/2 in. H) molds, and cured in a 100 percent relative humidity environment. Only the 1375°C material showed significant hardening.

To determine whether these results are due to the fly ash or to the processing, selected tests from the matrix in Table B-15 were made. Because there is some evidence that the particular fly ash obtained from Ohio Edison is not a good pozzolan, another ash was obtained from the Ft. Martin plant of the Monongahela Power Company. Both were tested for pozzolanic activity by an adaptation of ASTM C 595. The test mix used contains 1 part hydrated lime, 9 parts sand, and 1 part fly ash. Curing was done by holding the specimens in the molds for 24 hours at 23°C and then for 6 days at 55°C.

Both fly ashes showed pozzolanic activity, although much less than that required for use in blended hydraulic cements by ASTM C 595 (5.5 MPa or 800 psi). Inclusion of sand in the mix appears to increase compressive strength.

The next set of tests was made to explore the likelihood that cementitious reactions could occur under CAFB conditions. Grove limestone was ground to -149 μm and blended with Ohio Edison fly ash and with a potassium feldspar in the weight ratio of 1.79:1. The feldspar was passed through a shatter box to obtain a -200 mesh test material. The former mix was heated at 1375°C for 2-1/2 hours, the latter at 1070°C for 60 hours. We felt that these conditions bracketed the range of time-temperature combinations likely in the CAFB regenerator. Feldspar represented a possible impurity in limestone. The mixes were cooled, mixed with water to form thick pastes, and cast into cylinders 2.2 cm D x 2.5 cm H (0.860 in x 1.00 in). After moist curing for seven days, compressive strengths were determined (see Table B-16).

We then ran a series of tests to assess the pozzolanic activity of the ash and the reactivity of the CAFB gasifier bed residues. Mixes used were one part lime or bed residue to nine parts of Ottawa sand, plus one or two parts of fly ash. Five-cm cubes were cast and cured for

Table B-15

COMPRESSIVE STRENGTH OF FLY ASH/RESIDUE MIXES IN MPa

Fly Ash	Sand	Lime Source				
		Hydrated Lime	San Benito Residue		Abingdon Residue	
			As-Is	Ground	As-Is	Ground
Duquesne	No	-	No set	-	-	-
	No	-	-	-	No set	-
TUGCO	No	-	No set	-	-	-
Ohio Edison	No	1.07	-	-	-	-
	Yes(a)	1.45; 1.48	-	-	-	-
Ft. Martin	Yes	2.12; 1.90	-	-	-	-
	Yes	-	-	1.66; 1.69	-	-
	Yes	-	-	-	-	-
	Yes	-	-	-	-	-

[a] Sand mixes were 1 lime: 9 sand: 1 fly ash

Table B-16

COMPRESSIVE STRENGTH OF CYLINDERS CAST FROM HEAT-TREATED MIXES OF SILICA AND LIME-BEARING MATERIALS

Silica Source(A)	Lime Source		Silica/Lime Ratio, A/B	Heat Treatment	Compressive Strength	
	Source(B)	Condition			MPa	psi
Ohio Edison	Grove limestone	- 149 μm	1:1.79	1375°C, 2-1/2 hours	4.98, 4.62	670, 723
Feldspar[a]	Grove limestone	- 149 μm	1:1.79	1070°C, 60 hours	6.62	960

[a] Feldspar source is Spruce Pine, NC.

one day at ambient temperature (about 22°C) in sealed plastic bags and then for six days at 55°C + 3°C, still in sealed bags. Compressive strength data are in Table B-17.

The results can be summarized as follows:

- San Benito and Abingdon spent gasifier bed material show similar cementitious behaviors when mixed with Fort Martin fly ash. Compressive strengths are in the range of 0.48 to 0.76 MPa (70 to 110 psi) for mixes containing one part fly ash to one part lime, and 2.41 to 2.62 MPa (350 to 380 psi) for two parts of fly ash.

- Grinding the San Benito residue to -149 μm yielded intermediate strength with Fort Martin ash: 1.67 MPa (242 psi).

- Using hydrated lime as the lime source, strengths for mixes with one part of fly ash approached those for the mixes, above, with two parts fly ash: 1.90 to 2.12 MPa (275 to 308 psi). With two parts fly ash, strengths rose to 3.58 to 3.86 MPa (520 to 560 psi).

- With Ohio Edison and ground San Benito residue, strengths were only 1.17 MPa (178 psi), which was less than with Ft. Martin ash (1.67 MPa).

- With hydrated lime and Ohio Edison ash, strengths were less than with Ft. Martin ash, 1.46 vs 2.01 MPa (212 vs 292 psi). These results support the view that Ft. Martin ash is a better pozzolan than Ohio Edison and, therefore, a better medium to test the cementitious behavior of CAFB residues. The residues appear less reactive than fresh hydrated lime. Grinding the residues to -149 μm increases their reactivity somewhat.

- Both TUGCO fly ash and Pennsylvania Electric Company (Keystone plant) fly ash appear to be as good pozzolans as the Ft. Martin fly ash. Compressive strengths for pairs of 5-cm cubes averaged 4.24 MPa for the TUGCO and 4.65 MPa for the Keystone fly ash (615 and 595 psi), versus 3.72 MPa (540 psi) for the Ft. Martin fly ash.

- With TUGCO ash and ground San Benito residue, compressive strengths were somewhat lower - 3.68 MPa (535 psi) - than the above values, but much higher than for the Ft. Martin/San Benito mixes - 1.67 MPa (242 psi). This increase in strength is attributed partly to grinding the bed residue, but mainly to the higher ratio of fly ash to lime (2:1 vs 1:1). These results suggest that excess free lime, even as hydrated lime, is deleterious to bonding.

Table B-17

COMPRESSIVE STRENGTHS OF 5-cm CUBES CAST FROM FLY ASH/SPENT SORBENT MIXES[a], MPa (psi)

Lime Source and Condition	Fly Ash Source				
	Ft. Martin	Keystone	Ohio Edison	TUGCO	Boiler Fines
San Benito Gasifier Bed					
As is					
2:1[b]	2.62, 2.55 (380,370)	-	-	-	-
1:1	0.76, 0.76 (110,110)	-	-	-	-
Ground to -149 μm					
2:1	-	-	-	3.65, 3.72 (530,540)	4.28, 4.55 (620, 660)
1:1	1.65, 1.69 (240,245)	-	1.17, 1.17 (170,170)	-	-
Abingdon Gasifier Bed					
As is					
2:1	2.41, 2.48 (350,360)	-	-	-	-
1:1	0.48, 0.76 (70,110)	-	-	-	-
Lime					
2:1	3.86, 3.58 (560,520)	4.00 4.21 (580,610)	-	4.14, 4.34 (600,630)	-
1:1	2.12, 1.90 (308,275)	-	1.45, 1.48 (210,215)	-	-

[a]All mixes contain nine parts Ottawa sand to one part of the indicated lime, plus one or two parts of fly ash, as noted.

[b]Fly ash/lime ratio.

- With CAFB boiler fines and ground San Benito bed residues, strengths were higher than for TUGCO ash and ground residue - 4.41 MPa (640 psi)vs 3.68 MPa (535 psi).

REFERENCES

B-1. Taylor, H. F. W., The Chemistry of Cements, Volume 2, Chapter 16, The Academic Press, New York, NY, 1964.

APPENDIX C

ENVIRONMENTAL IMPACT STUDIES

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APPENDIX C

ENVIRONMENTAL IMPACT STUDIES

INTRODUCTION

The environmental impact studies reported here represent a continuation of earlier studies[1] on solid residues from the CAFB pilot plant at the Esso Research Centre, Abingdon, England (ERCA). These residues included solids taken from the gasifier, the regenerator, the cyclone, and the stack. Materials processed by dry sulfation, dead-burning, room-temperature ash blending, hot pressing, and slurry carbonation were also tested. Unprocessed CAFB residues were concluded to be environmentally unacceptable for direct land disposal, but processed residues, especially those subjected to high temperatures, could be acceptable. The major environmental concerns for leachates from CAFB residues were identified as pH, total dissolved solids (TDS), sulfide, sulfate, calcium, and heat release from the residues on contact with water. Trace elements did not appear to present a problem, nor was there any significant organic contamination. It was recommended that these conclusions be reassessed through tests on representative samples from a larger plant when available.

Tests were subsequently conducted on two sets of materials. One set, obtained in January 1980, included gasifier bed residues from a test run on lignite in the San Benito, Texas, demonstration plant and conventional lignite ash from the Texas Utility Generation Company (TUGCO). A later set was from Run 5, in which both residual oil and Texas lignite were used as fuels, supplemented by another conventional Texas lignite ash sample and residue from the RESOX unit. The total time of lignite feed was less than 10 hours before the test was terminated because of operational difficulties.

APPROACH

The impact studies covered four areas:

- o Residue characterization
- o Leaching behavior
- o Thermal activity
- o Assessment of RCRA impact.

Work in the first three areas used the environmental impact screening methodology developed under the previous contract.[C1] Since the completion of that work, several key RCRA regulations have been promulgated. The tests specified under these regulations were performed on the current residues and the results evaluated to determine the RCRA classification of CAFB residues and to assess the impact of RCRA regulations on disposal of CAFB residues.

TESTS ON JANUARY 1980 RESIDUES

Residue Characterization

Physical

The CAFB bed material from the San Benito plant was from the gasifier, which was operated in an oxidation mode following gasification of the lignite to simulate the regenerator, since the regenerator was not in operation. Table C-1 shows the particle size distribution by sieve analysis for the gasifier bed material. About 90 percent is in the range of 2360 to 500 μm, the 50 percent point is about 1100 μm. Some attrition has occurred since the feed limestone is typically 6350 (1/4 in.) x 300 μm.

Table C-2 shows the size distribution by TV image analysis for the lignite ash. The 50 percent point was estimated from a plot on arithmetic probability paper as 3.5 μm. A number mean of 5.68 μm can be calculated from the arithmetic average size for each size range, if one assumes the largest range is 50 to 55 μm.

Table C-1

PARTICLE SIZE DISTRIBUTION OF SAN BENITO CAFB GASIFIER BED MATERIAL BY SIEVE ANALYSIS

	Weight %	
Particle Size, μm	Incremental	Cumulative
>4000	0.24	0.24
3350-4000	0.47	0.71
2360-3350	4.93	5.64
2000-2360	4.93	10.57
1700-2000	7.43	18.00
1400-1700	10.12	28.12
1180-1400	11.98	40.10
1000-1180	14.1	54.20
600-1000	34.1	88.30
500- 600	6.32	94.62
425- 500	1.61	96.23
150- 425	1.94	98.17
75- 150	1.51	99.68
< 75	0.32	100.00

Table C-2

PARTICLE SIZE DISTRIBUTION OF TUGCO LIGNITE FLY ASH BY TV IMAGE ANALYSIS

Size Range, µm	No. of Particles	% of Particles
0- 5	1043	63.3
5-10	368	22.4
10-15	130	7.9
15-20	62	3.8
20-25	22	0.5
25-30	9	0.5
30-35	4	0.2
35-40	4	0.2
40-45	1	0.1
45-50	2	0.1
>50	4	0.2
Total No. Particles Counted	1649	
Mean Particle Size, µm	5.68	

X-Ray Diffraction

X-ray diffraction indicated that the San Benito gasifier bed material consists of $CaSO_4$, $Ca(OH)_2$, $CaCO_3$, and CaO, in decreasing order of concentration. The large amount of $CaSO_4$ is attributed to oxidation of CaS during operation of the gasifier in the oxidizing mode. The presence of $Ca(OH)_2$ is not surprising because of the ease with which CaO hydrates during solid handling in moist air. The TUGCO lignite ash was found to consist largely of SiO_2 (quartz) and a trace amount of α-Fe_2O_3 (hematite).

Surface Characteristics

Figure C-1 is an SEM of the San Benito bed material revealing cracks on the particle surface. The EDX scan shows the presence of Ca, S, and Si, agreeing with the x-ray diffraction results. Figure C-2 is an SEM of the TUGCO lignite fly ash revealing cenospheres ranging in size from submicron to 20 µm. EDX shows the presence of Si, Al, Ca, K, Ti, and Fe, as would be expected in lignite ash.

Leaching Behavior

Major Species

Both residues were subjected to leach tests using two leach media: deionized water and buffered acetic acid (pH 4.2). The acidic medium was made by dissolving 3.7 g of sodium acetate and 4.9 g of glacial acetic acid in 1 ℓ of deionized water. This was intended to simulate an acidic leaching environment, such as where codisposal of industrial, utility, and municipal wastes is practiced. Both continuous and intermittent shake tests were performed.

Tables C-3 and -4 summarize the major species found in the leachates. Table C-3 indicates the following for the spent bed material from the San Benito gasifier.

- The leachates were very similar to those we reported previously for the CAFB residue from the tests using residual

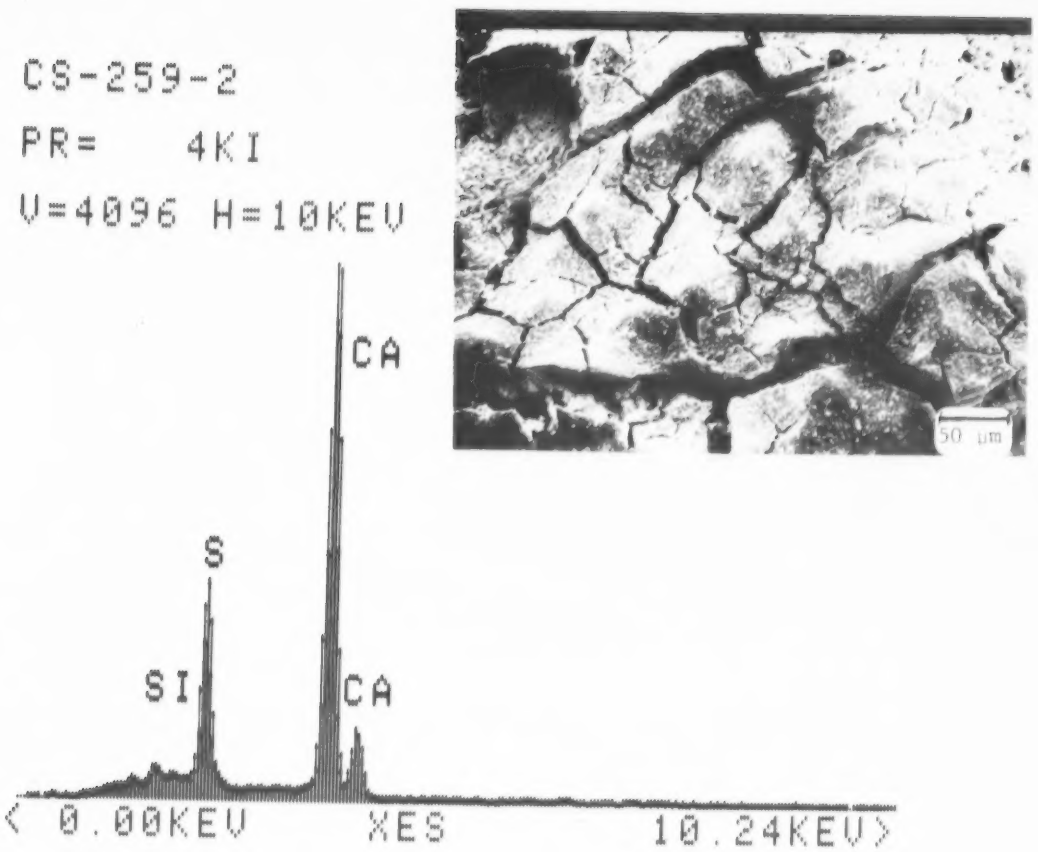

Figure C-1 -- SEM and EDX of CAFB Gasifier Bed Material from San Benito Plant

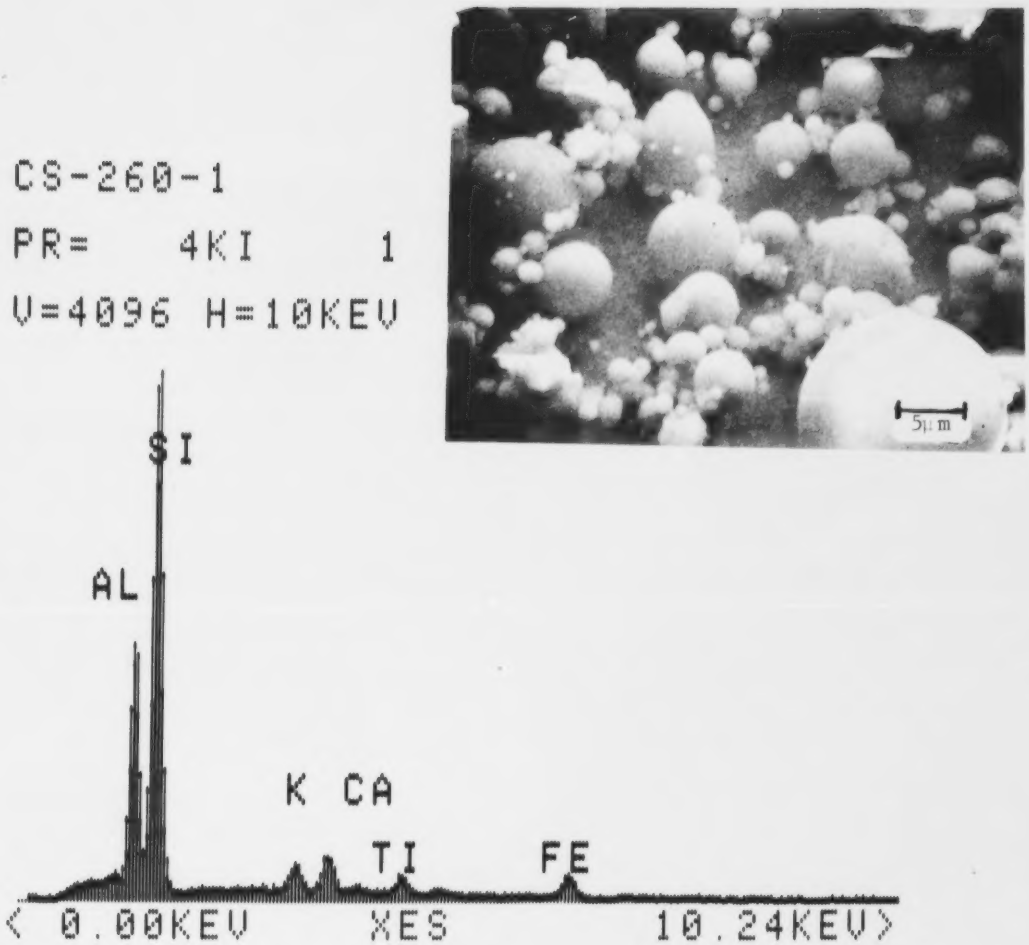

Figure C-2 -- SEM and EDX of a Texas Lignite Ash from TUGCO

Dwg. 1715872

Table C-3

LEACHATE CHARACTERISTICS OF SAN BENITO CAFB GASIFIER BED MATERIAL

Leaching Medium	Chemical Characteristics	Intermittent Shake, No. of 72-hr Intervals (S/L = 1/3)										Continuous Shake/hr (S/L = 1/10)	
		1	2	3	4	5	6	7	8	9	10	200	400
Deionized Water	pH	11.75	11.65	11.8	11.82	11.72	11.73	11.75	11.78	11.65	11.61	11.78	11.7
	Sp. Conductance millimho/cm	8.96	9.08	9.14	8.62	8.63	8.32	8.48	8.82	8.89	9.31	9.44	9.22
	Ca, mg/ℓ	1392	1448	1416	1376	1372	1356	1504	1424	1392	1396	1464	1584
	Mg, mg/ℓ	12	<10	<10	<10	16.8	12	<10	<10	<10	<10	19.2	14.4
	$SO_4^=$, mg/ℓ	1225	1247	1060	1175	1060	1352	1445	1410	1427	1667	1445	1380
	$S^=$, mg/ℓ	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	14.4
$NaC_2H_3O_2/HC_2H_3O_2$ Buffer pH = 4.5 Sp. Cond = 2.86 millimho/cm	pH	11.74	11.73	11.85	11.8	11.75	11.79	11.8	11.78	11.65	11.68	11.8	11.81
	Sp. Conductance millimho/cm	14.4	13.5	13.8	12.9	12.7	12.3	12.2	12.3	12.1	12.5	15.6	13.9
	Ca, mg/ℓ	3088	3088	3028	2952	2920	2888	3044	2840	2808	2952	3088	3256
	Mg, mg/ℓ	<10	40	26.4	<10	<10	24	26.4	19.2	<10	14.4	<10	28.8
	$SO_4^=$, mg/ℓ	1297	1225	876	1010	1297	1272	1225	1272	1000	1272	1510	1272
	$S^=$, mg/ℓ	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	15.6	14.4

oil at Abingdon. The leachates had high pH, Ca, SO_4, and TDS. The only exception was that, as expected, the leachate generated from the San Benito bed material had very little sulfide. Sulfide formed during lignite gasification would have been converted to sulfate or lost as SO_2 during operation in the oxidizing mode. The conversion to sulfate would not be typical in a commercial CAFB plant.

- Leachate quality produced by deionized water was about the same after ten 72-hour intervals of intermittent leaching as after the first interval. For continuous leaching, TDS, Ca, Mg, and SO_4 peaked at 200 hours but at 400 hours were still higher than the initial values; pH was essentially constant.
- Leaching with buffered acetic acid had no effect on leachate pH (pH = 11.8) because the pH was dominated by the extremely alkaline spent bed material. TDS declined in the intermittent leaching by about 15 percent but was essentially constant in the last five cycles. Ca declined about 7 percent but also appeared to have leveled off. Values for $SO_4^=$ and $S^=$ were unchanged throughout, while Mg values fluctuated in the range of <10 to 40 mg/ℓ. For continuous leaching, TDS, $SO_4^=$, and $S^=$ peaked at 200 hours, while Ca rose about 5 percent in 400 hours. Mg tripled in 400 hours, but this behavior may be similar to the fluctuations observed in intermittent leaching. Sulfite was higher than in the intermittent leaching.

Table C-4, which presents leachate data for TUGCO lignite ash, shows the following:

- Initial leachates produced in intermittent leaching with both media showed high Ca and SO_4, with rapid declines to low levels as leaching continued. The response of Mg was similar but also showed the same fluctuations as the leachates from the bed residues. Values for pH approached those of the leaching medium.
- In continuous leaching with deionized water, values at 400 hours were about the same as at 200 hours, except for Ca, which showed a sharp increase (3x), and Mg, which showed a sharp decrease. With buffered acid, values at both times were about the same, although Ca and Mg both increased 15 percent.

Trace Elements

Table C-5 presents data on major, minor, and trace elements in both solid residues and in the 200-hour leachates produced from them.

Table C-4

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LEACHATE CHARACTERISTICS OF TEXAS LIGNITE ASH FROM TUGCO

Leaching Medium	Chemical Characteristics	Intermittent Shake, No. of 72-hr Intervals (S/L = 1/3)										Continuous Shake/hr (S/L = 1/10)	
		1	2	3	4	5	6	7	8	9	10	200	400
Deionized Water	pH	8.89	8.5	8.71	8.35	8.25	8.19	8.16	8.1	7.9	7.4	9.4	8.21
	Sp. Conductance millimho/cm	1.45	0.44	0.24	0.23	0.16	0.13	0.12	0.11	0.12	0.1	0.61	0.61
	Ca, mg/ℓ	340	120	36	28	20	<10	<10	<10	<10	<10	88	280
	Mg, mg/ℓ	16.8	<10	<10	19.2	19.2	14.4	<10	<10	<10	<10	21.6	<10
	$SO_4^=$, mg/ℓ	602.5	120.5	27.9	15.3	24.1	< 10	15.3	13.5	12	<10	212	213.7
	$S^=$, mg/ℓ	<10	-	-	-	-	-	-	-	-	-	<10	<10
$NaC_2H_3O_2/HC_2H_3O_2$ Buffer pH = 4.5 Sp. Cond = 2.86 millimho/cm	pH	5.75	4.62	4.15	4.6	4.6	4.58	4.78	4.55	4.52	4.35	4.75	4.87
	Sp. Conductance millimho/cm	7.77	4.76	4.55	4.08	3.67	3.68	4.27	3.68	3.78	3.53	5.28	4.87
	Ca, mg/ℓ	1552	552	260	128	92	84	316	104	56	28	640	736
	Mg, mg/ℓ	201.6	91.2	141.6	45.6	36	24	62.4	43.2	<5	288	100.8	115.2
	$SO_4^=$, mg/ℓ	940	82.5	12	<10	<10	<10	<10	<10	<10	<10	279	252
	$S^=$, mg/ℓ	<10	-	-	-	-	-	-	-	-	-	15.6	<10

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Table C-5

CHARACTERISTICS OF SAN BENITO CAFB GASIFIER BED MATERIAL AND TUGCO LIGNITE ASH AND THEIR LEACHATES

Substance	San Benito CAFB Bed			TUGCO Lignite Ash			MCL, mg/ℓ
	Solid, ppm	Leachate Deionized H_2O, mg/ℓ	Leachate Acetic Buffer, mg/ℓ	Solid, ppm	Leachate Deionized H_2O, mg/ℓ	Leachate Acetic Buffer mg/ℓ	
Al	0.57%	<0.2	<0.2	6.2%	5	>50	
Ag	<1	<0.02	<0.02	<1	<0.02	<0.02	0.05
As		<0.001	<0.001		0.0075	0.11	0.05
B	10	0.05	<0.05	500	15	15	
Ba	300	<1	<1	1000	<1	<1	1.0
Be	<1	<0.01	<0.01	5	<0.01	<0.01	
Bi	<10	<0.05	<0.05	<10	<0.05	<0.05	
Ca	46.9%	1464	3088	4.79%	88	640	200
Cd	<10	<0.05	<0.05	<10	<0.05	<0.05	0.01
Co	<10	<0.2	<0.2	10	<0.2	<0.2	
Cr	70	0.1	0.07	100	0.55	0.6	0.05
Cu	20	<0.5	<0.5	200	<0.5	0.8	1.0
Fe	0.69%	<0.3	<0.3	2.05%	<0.3	50	0.3
Ga	<20	<0.05	<0.05	100	0.08	<0.2	
Ge	<10	<0.1	<0.1	10	<0.1	0.15	
Hg		<0.0005	<0.0005		<0.0005	<0.0005	0.002
K	0.09%			0.59%			
Mg	0.36%	19.2	<3	0.96%	21.6	100.8	150
Mn	2000	<0.05	<0.05	1000	<0.05	2	0.05
Mo	<10	<0.05	<0.05	20	1.5	0.5	
Na	0.03%	~5	>>50	0.22%	<5	>>50	
Ni	50	<0.1	<0.1	50	<0.1	<0.1	2.0
Pb	<20	<0.05	<0.05	200	<0.05	<0.05	0.05
Sb	<100	<0.5	<0.5	<100	<0.5	<0.5	
Se		<0.001	<0.001		0.17	0.12	0.01
Si	1.81%	<1	<1	28.15%	<1	>50	
Sn	<30	<0.1	<0.1	<30	<0.1	<0.1	1.0
Sr	>2000	>50	>50	2000	2	10	
Ti	200	<0.5	<0.5	>2000	<0.5	2	
V	500	<0.05	<0.05	500	0.7	0.5	
Zn	<100	<2	<2	<100	<2	<2	5.0
Zr	<20	<0.1	<0.1	700	<0.1	<0.1	
SO_4	11.48%	1445	1510	2.73%	212	279	250
$S^=$	0.03%	<10	15.68	0.03	<10	15.68	
F		1.8	<1		2.3	<1	2.4
Cl		38	39		4	28	250
NO_3 (as N)		<10	<10		<10	<10	10
PO_4		<10	<10		<1	<1	
TOC		<5	-		<5	-	
pH		11.78	11.8		9.4	4.75	6.5 to 9.2
SC, μmho/cm		9440	15600		610	5280	~750

[a] MCL - Maximum Containment Levels. Based on NIPDWR, NSDWR, [a] USPHS Standards, and WHO

Exceeds DWS

Exceeds 10 x DWS

The leachate concentrations using deionized water and buffered acetic acid are compared with DWS and 100 X DWS for perspective. The following points can be noted:

- Trace elements in the San Benito bed material were low, as previously reported[1] for CAFB residues. The Cr in both San Benito leachates using lignite fuel, however, exceeded the DWS, unlike the previously tested CAFB spent bed materials (using residual oil) whose leachates passed all DWS for heavy metals.
- The leachates from conventional lignite ash had higher concentrations of trace elements than did the CAFB leachates. Cr and Se and, perhaps Ca, exceeded DWS, but not 100 X DWS. This finding is in agreement with the that from another TUGCO lignite ash sample reported previously.[C1] In the acidic leachate Fe exceeded 100 X DWS while Mn was about 40 X DWS. Other trace elements were also higher: Al, As, Cu, Ga, Ge, Na, Si, Sr, Ti, $S^{=}$, and Cl.

THERMAL ACTIVITY

We employed the standard thermal activity screening tests developed under the previous contract.[1] The San Benito gasifier bed material released a significant amount of heat on contacting water, quantitatively in the same range as the spent CAFB bed materials from the residual oil runs. The TUGCO lignite ash from the conventional boiler showed little residual thermal activity. Table 6 summarizes the results.

Table C-6

THERMAL ACTIVITY SUMMARY

Sample	Solid/Water	ΔT_{max}, °C	Time to Reach T_{max}, min
San Benito Bed	3g/20 mℓ	12	20
"	16g/4 mℓ	>75	<1
TUGCO Ash	3g/20 mℓ	<0.2	--
"	16g/4 mℓ	<0.2	--

Assessment of RCRA Impact

The Resource Conservation and Recovery Act (RCRA) is the major law regulating solid waste disposal. According to the Phase I regulations on hazardous waste management (RCRA Subtitle C), as promulgated by EPA on May 19, 1980, a waste can be classified as hazardous by either of two mechanisms (Figure C-3): by being on EPA's hazardous waste lists or by possessing any of the hazardous characteristics (corrosivity, ignitability, reactivity, and toxicity). CAFB residue is not on the EPA hazardous waste lists, so it should be categorized as specified on the left half of Figure C-3. The CAFB residue is neither corrosive nor ignitable according to the RCRA definitions. To determine its toxicity, the EPA extraction procedure (EP) was performed on the San Benito bed material as well as on the TUGCO lignite ash. Table C-7 summarizes the RCRA/EP results, including tests required by RCRA on eight trace elements and other parameters of specific interest for CAFB residue and lignite ash. Results indicated that both materials were nontoxic when compared with the criteria -- 100 times the maximum contaminant levels for community water systems (NIPDWR). The CaO and residual CaS, however, in a typical unprocessed CAFB residue may cause it to be classified as reactive and, thus, hazardous under the RCRA definition. CAFB residue should therefore be investigated further when a more representative residue is available.

One important point is that utility wastes from fossil-fuel-burning processes are temporarily exempt from the Phase I hazardous waste regulations. Whether the CAFB residues from fossil-fuel "gasification" processes are included in the exemption is not yet clear. EPA plans to develop specific standards in Phase II and Phase III, applicable to fossil-fuel processes that will incorporate more flexible, site-specific factors.

Should the CAFB residue (processed or unprocessed) be determined to be merely a solid waste, it still must be disposed of in a "sanitary landfill" according to RCRA Subtitle D. Criteria for sanitary landfills

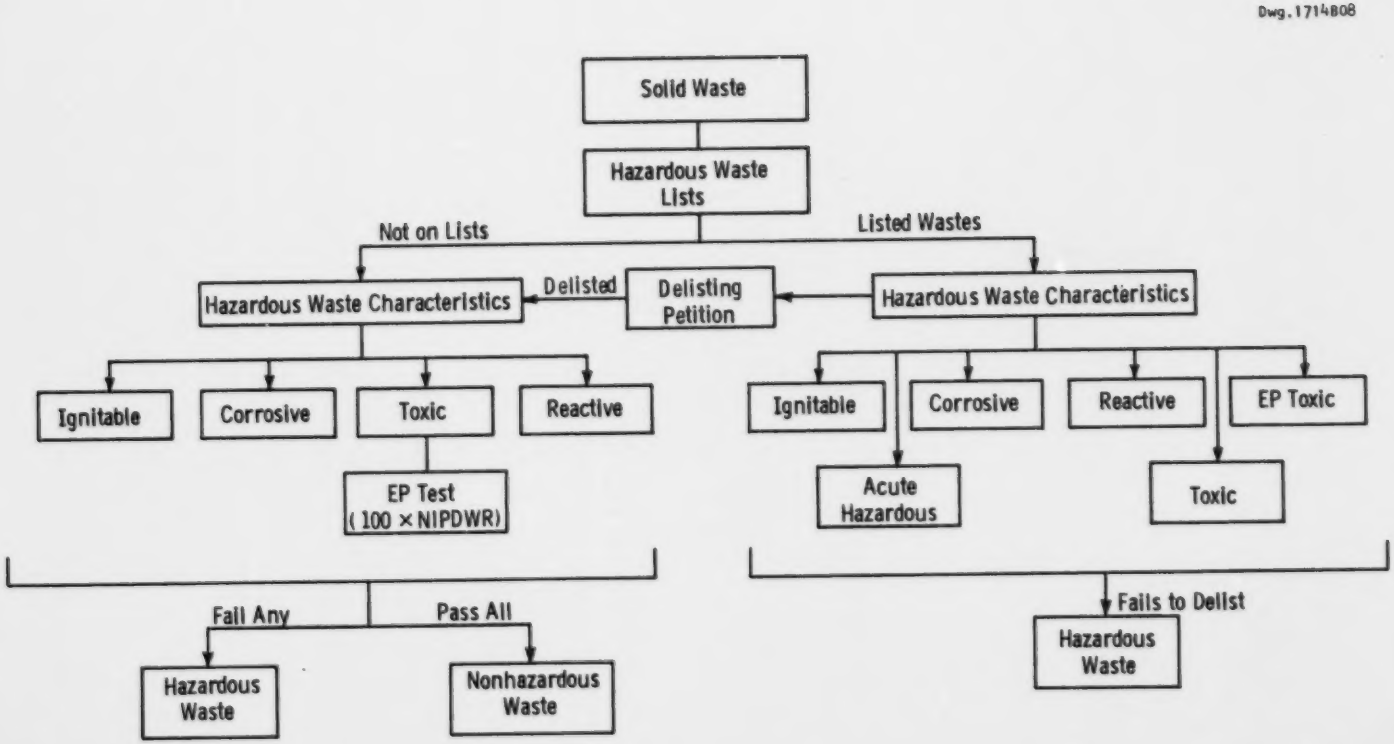

Figure C-3 -- Hazardous waste identification mechanism

Table C-7

SUMMARY OF RCRA/EP TOXICITY TEST ON SAN BENITO CAFB GASIFIER RESIDUE AND TUGCO LIGNITE ASH

Parameters	EP Leachate, ppm		RCRA Criteria, ppm
	CAFB Residue	Lignite Ash	
Ag	<0.02	<0.02	5.0
As	<0.001	0.003	5.0
Ba	<1	<1	100.0
Cd	0.005	0.014	1.0
Cr	0.09	0.28	5.0
Hg	0.0014	0.0021	0.2
Pb	<0.02	<0.02	5.0
Se	<0.001	0.013	1.0
Ca	3408	208	
Mg	<10	29	
$S^{=}$	42	26	
SO_4	1410	1040	
Specific Conductance, µmho/cm	12800	1050	
Total 0.5N Acetic Acid Added, mℓ	400	63	
Final pH	12.0	4.98	

and groundwater were promulgated in the Federal Register on September 13, 1979.[a]

Table C-8 summarizes the San Benito CAFB leachate characteristics using deionized water by the 200-hour shake method, which projects a worst-case potential contamination release without the benefit of soil attenuation and dilution. The current maximum contaminant levels (MCL) for underground drinking water sources (the primary MCL:NIPDWR)[b] and the proposed additional criteria for public water systems (the secondary MCL:NSDWR)[c] are listed for comparison. Table C-8 indicates the following for this worst case leachate:

- Trace elements for which regulatory levels have been proposed are below those levels for most MCLs (Ag, As, Ba, Hg, Pb, and Se) and all SMCLs (Cu, Fe, Mn, Cu, Zn). Leachate Cr from the San Benito bed material resulting from lignite fuel is 0.1 ppm, slightly higher than the PMCL of 0.05 ppm. Cd in the leachate (< 0.05 ppm) may be higher than the PMCL (0.01 ppm). We expect both would be reduced by soil attenuation and dilution.
- Leachate pH, SO_4, and TDS exceed SMCLs. Interaction with soils such as montmorillonite and kaolinite clays, which have significant attenuation capacities, may reduce the leachate pH, but dilution before and after entering the groundwater may be needed.
- Nitrate and chloride are lower than the respective PMCLs without dilution, and thus, should be no problem.
- Fluoride meets the regulatory level only if the annual average of the maximum daily air temperature is below 21.4°C.
- Sulfide odor from the CAFB leachate may cause environmental concern.
- Color and foaming agents, which are in the NSDWR, are not expected to cause problems, since the CAFB leachates are generally colorless and are not known to contain foaming agents.

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[a] Reference 2. Part 257
[b] Reference 2. Section 257.3-4 and Part 141, Subpart B
[c] Reference 2. Part 143, Section 143.3

Table C-8

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COMPARISON OF THE SAN BENITO CAFB GASIFIER BED LEACHATE CHARACTERISTICS AND THE UNDERGROUND DRINKING WATER SOURCE (UDWS)

Substance	San Benito CAFB Leachate ppm	Groundwater Criteria, ppm	
		Current: NIPDWR	Proposed Additions: NSDWR
Al	< 0.2		
Ag	< 0.02	0.05	
As	< 0.001	0.05	
B	0.05		
Ba	< 1	1.0	
Be	< 0.01		
Bi	< 0.05		
Ca	1464		
Cd	< 0.05	0.01	
Co	< 0.2		
Cr	0.1	0.05	
Cu	< 0.5		1.0
Fe	< 0.3		0.3
Hg	< 0.0005	0.002	
Mg	< 30		
Mn	< 0.05		0.05
Mo	< 0.05		
Na	5.		
Ni	< 0.1		
Pb	< 0.05	0.05	
Sb	< 0.5		
Se	< 0.001	0.01	
Si	< 1		
Sn	< 0.1		
Sr	> 50		
Ti	< 0.5		
V	< 0.05		
Zn	< 2		5.0
Zr	< 0.1		
SO_4	1445		250
Cl	38		250
F	1.8	1.4-2.4	
NO_3 (as N)	< 10	10.0	
TOC	< 10		
pH	11.8		6.5 - 8.5
TDS	> 2000		500
Specific Conductance millimho/cm	9.4		
Color	None		15 Color Units
Odor	None[a]		3 Threshold Odor Number
Foaming Agents	None		0.5
Radioactivity	Not Determined[b]	5 p Ci/ℓ Ra 226 & 228	
Biological Activity	None	4 Coliform/ 100 mℓ	

Exceed MCL (Maximum Contamment Levels)

[a] Sulfide odor must be determined on a more representative sample

[b] Expected to be similar to conventional power plant residue, if any

- Radionuclides (Ra-226, Ra-228) and gross α-particle radioactivity were not tested in this study for several reasons. We expect their levels to be similar to or less than those in leachates from conventional power plant residues. The regulations on radionuclides, however, apply only to community water systems and so the possible contaminant levels in the leachates should be compared to background values in such water systems and not merely at the boundaries of the diposal facility. Finally, most U.S. coals do not have significant radionuclide content, so this parameter needs to be checked only on a site-specific basis.

- Microbiological contaminant in the San Benito and TUGCO leachates was tested by the Westinghouse Biological Group. No coliform bacteria was found in either leachate tested. Both the high CAFB process temperature and the highly alkaline leachate are factors contributing to zero microbiological activity.

- The low Cd content in CAFB solid and the high pH of leachate suggest that the Cd standard for annual agricultural application (application rate no more than 0.5 kg per hectare on land used for production of tobacco, leafy vegetables or root crops grown for human consumption)[a] can be met without difficulty. The cumulative application may not exceed 5 to 20 kg/ha, however, depending on the soil cation exchange capacity and provided that the soil pH is over 6.5.

TESTS ON RUN 5 RESIDUES

Residue Characterization

X-Ray Diffraction

X-ray diffraction identification of molecular species in the residues are summarized in Table C-9. The species found are in accord with expectations for normal operation of the CAFB process except for failure to show trace to minor amounts of CaS in the regenerator bed material. The RESOX residue is a partially consumed coal and should show typical ash constituents.

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[a] Reference C2. Part 257 Section 257.3-5(a)(1)(ii)

Table C-9

X-RAY DIFFRACTION IDENTIFICATION OF
SAN BENITO CAFB RESIDUES

San Benito Residue	X-ray Diffraction
Gasifier Bed	Major: CaO Minor: CaS Trace: $Ca(OH)_2$, $CaSO_4$
Regenerator Bed	Major: CaO Minor: $Ca(OH)_2$
RESOX	Major: Amorphous SiO_2, quartz Trace: Al_2O_3

Surface Characteristics

The SEM and EDX results are presented in Figures C-4 and C-5. Figure C-4 shows SEM and EDX of the regenerator material identifying two types of particles - particle 1 being predominantly $CaSO_4$ and CaS; and particle 5 being largely $Ca(OH)_2$ and CaO, with the latter having been partially hydrated and physically disintegrated (as the photo indicates) to $Ca(OH)_2$. Figure C-5 shows RESOX material, which is a coallike material containing approximately 60 percent unburned carbon. The EDX shows its mineral content to be primarily from ash.

Leaching Behavior

Major Species

Standard Westinghouse leaching tests were carried out, and results are presented in Tables C-10 and C-11 for the bed materials. Table C-10 shows the following for the regenerator material:

- Ca, SO_4, S, and TDS are high initially and decrease with continued leaching. This is shown clearly in the intermittent leaching and indirectly for the continuous leaching by the smaller (0 to 35 percent) increase in the second 200 hours.
- Use of buffered acetic acid instead of deionized water increased Ca and TDS but not pH, Mg, SO_4, or S.
- Sulfide was confirmed, although it had not been detected by x-ray diffraction.
- Mg levels fluctuated in a declining trend for deionized water leaching and a zero trend for acidic leaching.

Table C-11 shows similar results for the gasifier bed material, although values for TDS, Ca, and SO_4 are higher. Sulfide is higher initially, while pH and Mg are about the same as in Table C-2.

Trace Elements

Table C-12 shows 200-hour continuous leaching results for major, minor, and trace elements in leachates from the two bed materials. Although these results are generally similar to these in Table C-5,

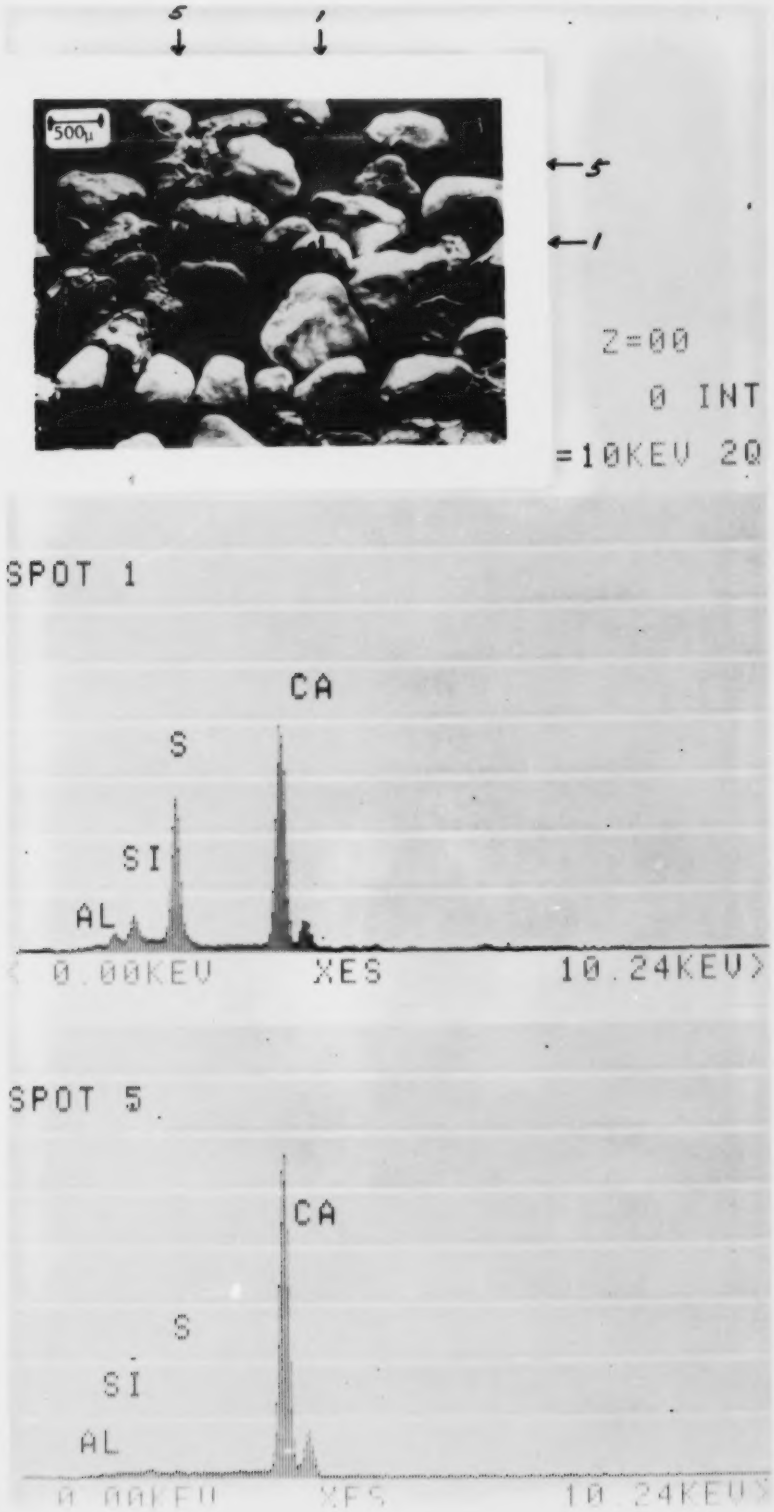
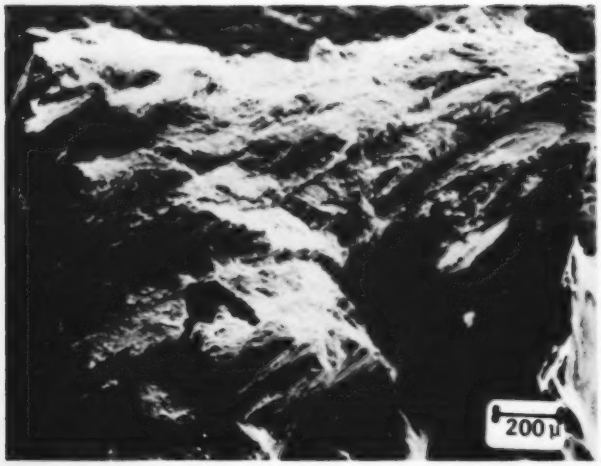
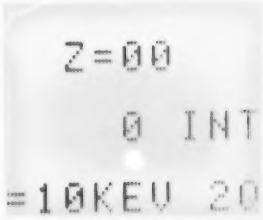


Figure C-4 -- SEM and EDX of CAFB regenerator bed material from San Benito run 5





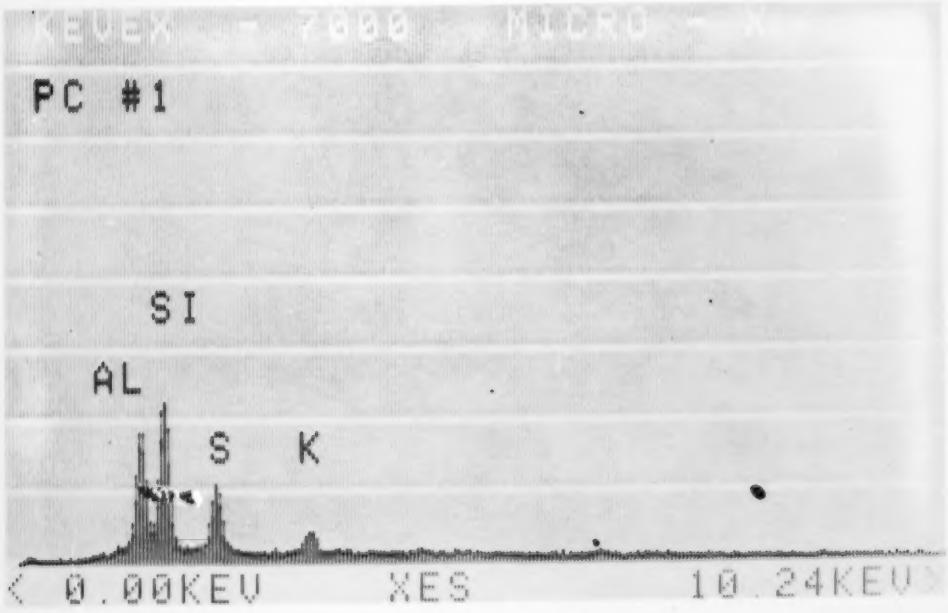


Figure C-5 -- SEM and EDX of RESOX ash from San Benito run 5.

Table C-10

LEACHATE CHARACTERISTICS OF SAN BENITO RUN 5 REGENERATOR BED MATERIAL

Leaching Medium	Chemical Characteristics	Intermittent Shake, No. of 72-hr Intervals (S/L = 1/3)										Continuous Shake/hr (S/L = 1/10)	
		1	2	3	4	5	6	7	8	9	10	200	400
Deionized Water. pH = 7	pH	11.89	11.87	12.18	12.12	12.21	12.3	12.25	12.33	12.31	12.35	12.23	12.21
	Sp. conductance µmho/cm	9.72	11	12.4	11.2	9.18	8.62	8.43	8.22	7.88	7.55	10.1	10.92
	Ca, mg/l	2280	2240	3016	2338	1700	1508	1316	1184	1088	922	1852	2272
	Mg, mg/l	55.2	129.6	24	26.4	12	16.8	19.2	24	14.4	16.8	31.2	14.4
	$SO_4^=$, mg/l	1445	1547.5	2570	2067.5	1410	1127.5	885	673.7	470	370	1272.5	1200
	$S^=$ mg/l	896	1072	1072	816	512	368	256	184	128	79.04	1056	1445
$NaC_2H_3O_2/HC_2H_3O_2$ Buffer. pH = 4.45 cond = 3.2 µmho/cm	pH	11.99	11.9	12.12	12.08	12.18	12.2	12.25	12.26	12.22	12.2	12.15	12.15
	Sp. conductance µmho/cm	13.2	16.2	17.3	16.2	14.3	13.5	13.3	12.8	12.9	12.4	16.1	17
	Ca, mg/l	4048	3808	4472	3952	3352	2960	2750	2600	2656	2568	3880	4344
	Mg, mg/l	19.2	43.2	33.6	28.8	19.2	48	57.6	48	14.4	19.2	38.4	122.4
	$SO_4^=$, mg/l	1300	1150	1555	1300	1085	1030	752.5	440	300	265	984	1248
	$S^=$ mg/l	848	864	1008	816	528	288	240	192	144	76	1625	1735

Table C-11

LEACHATE CHARACTERISTICS OF SAN BENITO RUN 5 GASIFIER BED MATERIAL

Leaching Medium	Chemical Characteristics	Intermittent Shake, No. of 72-hr Intervals (S/L = 1/3)										Continuous Shake/hr (S/L = 1/10)	
		1	2	3	4	5	6	7	8	9	10	200	400
Deionized Water. pH = 7	pH	11.9	11.82	12.12	12.12	12.23	12.3	12.23	12.31	12.28	12.32	12.28	12.3
	Sp. conductance µmho/cm	12.7	13.9	14.4	11.7	9.96	9.07	9.2	8.68	8.57	8.24	11.9	12.8
	Ca, mg/l	3416	3688	3896	2568	1988	1784	1600	1504	1512	1432	2520	3208
	Mg, mg/l	43.2	19.2	14.4	4.8	2.4	0	0	14.4	19.2	14.4	9.6	45.6
	$SO_4^=$, mg/l	2717.5	2067.5	2330	1582.5	1622.5	1712.5	1325	1475	1410	1325	1448	1336
	$S^=$ mg/l	1144	1648	1432	896	568	392	288	192	136	88.16	1867.5	2570
$NaC_2H_3O_2/HC_2H_3O_2$ Buffer. pH = 4.45 cond = 3.2 µmho/cm	pH	12	11.95	12.12	12.12	12.17	12.2	12.22	12.28	12.12	12.18	12.2	12.18
	Sp. conductance µmho/cm	17.4	18.8	20	17.2	15.2	14.6	13.1	13.5	13.9	13.1	17.1	17.6
	Ca, mg/l	4944	4836	5724	4384	3608	3448	3076	3128	3240	3064	4160	4632
	Mg, mg/l	9.6	52.8	9.6	4.8	24	28.8	21.6	14.4	24	28.8	19.2	26.4
	$SO_4^=$, mg/l	1460	1395	1920	1490	1515	1502.5	975	1325	1410	1225	1168	1424
	$S^=$ mg/l	1056	1344	1464	960	576	256	256	144	128	71.44	1770	1060

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Table C-12

SOLID AND LEACHATE CHARACTERISTICS OF SAN BENITO RUN 5 RESIDUES BY 200 HR SHAKE TESTS

Substance	Gasifier Bed			Regenerator Bed			
	Solid ppm	Leachate Deionized H_2O, mg/l	Leachate Acetic Buffer, mg/l	Solid ppm	Leachate Deionized H_2O, mg/l	Leachate Acetic Buffer, mg/l	MCL, mg/l
Al	0.39%	<1	<1	0.45%	<1	<1	
Ag	<1	<0.01	0.02	<1	<0.01	<0.01	0.05*
As		0.001	<0.001		0.002	<0.001	0.05*
B	10	<1	<1	10	<1	<1	
Ba	10	<1	<2	10	<1	<2	1.0*
Be	<1	<0.01	<0.01	<1	<0.01	<0.01	
Bi	<3	<0.1	<0.2	<3	<0.1	<0.2	
Ca	58.4%	2520	4160	62.08%	1852	3880	200
Cd	<3	<0.01	<0.01	<3	<0.01	<0.01	0.01*
Co	<10	<1	<2	<10	<1	<2	
Cr	<3	<0.05	<0.2	<3	<0.05	<0.2	0.05*
Cu	5	<1	<1	5	<1	<1	1.0
Fe	0.55%	<1	<1	0.63%	<1	<1	0.3
Ga	<3	<3	<7	<3	<3	<7	
Ge	<10	<1	<1	<10	<1	<1	
Hg		<0.001	0.001		<0.0011	<0.001	0.002*
K	0.009%			0.002%			
Mg	0.57%	9.6	19.2	0.76%	31.2	38.4	150
Mn	1000	<0.2	<1	1000	<0.2	<1	0.05*
Mo	<10	<1	<2	<10	<1	<2	
Na	0.036%			0.009%			
Ni	300	<1	<1	300	<1	<1	2.0
Pb	<1	<0.05	<0.2	<1	<0.05	<0.2	0.05*
Sb	<10	<1	<2	<10	<1	<2	
Se		0.023	0.004		0.013	0.002	0.01*
Si	1.29%	5	<2	1.27%	5	<2	
Sn	<3	<1	<1	<3	<1	<1	1.0
Sr	<10			<10			
Ti	300	<1	<2	300	<1	<2	
V	5000	<1	<1	5000	<1	<1	
Zn	<30	<1	<2	<30	<1	<2	5.0
Zr	20			20			
SO_4	9.68%	1867.5	1770	4.2%	1272.5	1625	250
$S^=$	4.19%	1448*	1168*	2.32%	1056*	984*	
TOC		<10			<10		
pH		12.28	12.2		12.23	12.15	6.5 to 9.2
SC, μmho/cm		11900	17100		10100	16100	~750

MCL - NIPDWR*, NSDWR, and WHO Drinking Water Standards

Exceeds DWS

Exceeds 10 × DWS

there are several specific differences. Of the ten species in the NIPDWR, eight of which are indicated in Table C-12 by asterisks, only Se definitely exceeds the regulatory levels. Chromium and lead may exceed allowable levels; fluoride and nitrate were not measured.

Nickel and vanadium levels in the solids are much higher than in Table C-5 (300 vs 50 ppm for Ni and 5000 vs 500 ppm for V), reflecting the use of residual oil as fuel. However, these elements are apparently not readily leachable.

With regard to NSDWR, Fe and Mn may exceed proposed levels. TDS, Ca, and pH are high.

Table C-13 shows similar examinations of a second specimen of Texas lignite ash, designated in the table as No. 1. The No. 2 ash is the same one as in Table C-5 and is repeated for ease of comparison. Generally, the analytical results agree, indicating reproducibility, but again there are individual instances of wide variations. For the solids, Cd, Pb, Sb, Sn, Sr, and Ti show up in Ash No. 2 at at least twice the levels of Ash No. 1. The deionized water leachates tend to reflect this difference. In some cases the acidic leachates show higher levels of certain elements, notably As, Fe, and Mn. While the acidic leaching procedure was not exactly that of the EP toxicity test, we note that none of the levels exceeded 100 X PMCL. (The earlier criterion was 10 X PMCL, as noted in Table C-13).

Thermal Activity

Standard Westinghouse heat release tests were performed. Results indicated that heat release on contacting water would be an environmental concern, which is in agreement with the previous findings.

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2. Code of Federal Regulations, Title 40, July 1, 1980.

Dwg. 1718B36

Table C-13
SOLID AND LEACHATE CHARACTERISTICS OF TEXAS LIGNITE ASH* BY 200 HR SHAKE TEST

	Lignite Ash 1		Lignite Ash 2			
Substance	Solid, ppm	Leachate, Deionized Water, mg/ℓ	Solid, ppm	Leachate, Deionized H_2O, mg/ℓ	Leachate, Acetic Buffer mg/ℓ	MCL, mg/ℓ
Al	major	> 1	6.2%	5	> 50	
Ag	< 1	< 0.01	< 1	< 0.02	< 0.02	0.05 •
As	12.1	0.006		0.0075	0.11	0.05 •
B	500	> 1	500	15	15	
Ba			1000	< 1	< 1	1.0 •
Be	5	< 0.01	5	< 0.01	< 0.01	
Bi	< 10	< 0.01	< 10	< 0.05	< 0.05	
Ca	major	144	4.79%	88	640	200
Cd	< 3	< 0.01	< 10	< 0.05	< 0.05	0.01 •
Co	20	< 0.01	10	< 0.2	< 0.2	
Cr	80	0.7	100	0.55	0.6	0.05 •
Cu	200	< 1	200	< 0.5	0.8	1.0
Fe	major	< 0.1	2.05%	< 0.3	50	0.3
Ga			100	0.08	< 0.2	
Ge			10	< 0.1	0.15	
Hg	0.12	< 0.001		< 0.0005	< 0.0005	0.002 •
K			0.59%			
Mg	> 1000	< 10	0.96%	21.6	100.8	150
Mn	660	< 0.01	1000	< 0.05	2	0.05
Mo	30	0.2	20	1.5	0.5	
Na	> 1000	~ 1	0.22%	< 5	>> 50	
Ni	50	< 0.05	50	< 0.1	< 0.1	2.0
Pb	85	< 0.01	200	< 0.05	< 0.05	0.05 •
Sb	< 33	< 0.05	< 100	< 0.5	< 0.5	
Se	4.0	0.05	.	0.17	0.12	0.01 •
Si	major	< 1	28.15%	< 1	> 50	
Sn	< 10	< 0.05	< 30	< 0.1	< 0.1	1.0
Sr	1000	> 1	2000	2	10	
Ti	> 1000	< 1	> 2000	< 0.5	2	
V	250	0.5	500	0.7	0.5	
Zn	100	< 1	< 100	< 2	< 2	5.0
Zr		< 1	700	< 0.1	< 0.1	
SO_4		263	2.73%	212	279	250
S=		< 10	0.03	< 10	15.68	
F		< 1		2.3	< 1	2.4 •
Cl		< 1		4	28	250
NO_3 (as N)		< 1		< 10	< 10	10 •
PO_4		< 1		< 1	< 1	
TOC		< 10		< 5		
pH		10.7		9.4	4.75	6.5 to 9.2
SC, μmho/cm		810		610	5280	~ 750

DWS - • NIPDWR, NSDWR, USPHS, and WHO Drinking Water Standards

Exceeds DWS

Exceeds 10 × DWS

• Samples Obtained from a Texas Power Plant

APPENDIX D
SULFIDE OXIDATION TESTS

BACKGROUND AND OBJECTIVE

Calcium sulfide (CaS), the product formed in high-temperature limestone or dolomite desulfurization processes carried out under reducing conditions, is unsuitable for direct disposal since it may react with water, releasing hydrogen sulfide (H_2S) gas. An alternative to regenerating the CaS and recovering sulfur as in the CAFB process is the air oxidation of CaS in the gasifier effluent to calcium sulfate ($CaSO_4$). If the oxidation can be carried out completely with little liberation of sulfur dioxide (SO_2), this might permit a once-through sorbent option with an acceptable environmental impact.

The preferred oxidation, $CaS + 2O_2 \rightarrow CaSO_4$, occurs at temperatures above 400°C. Above 1090°C, oxidation that liberates SO_2 is thermodynamically favored,

$$CaS + 3/2\ O_2 \rightarrow CaO + SO_2.$$

The sulfide/sulfate reaction,

$$CaS + 3\ CaSO_4 \rightleftarrows 4\ CaO + 4\ SO_2,$$

will also liberate SO_2. Equilibrium SO_2 levels for this reaction are:[D1]

Temperature, °C	Equilibrium SO_2 Level, atm
727	$(1.81\text{-}2.61) \times 10^{-4}$
827	1.7×10^{-3}
927	0.25
1127	0.80

Sulfide oxidation, therefore, must occur at temperatures below 800°C. Most of the work on CaS oxidation has been conducted at temperatures higher than 1000°C to study CaO formation.[D2,D3]

Calcium sulfate has a larger molar volume (52.2 cc/mole) than does CaS (33.8) or $CaCO_3$ (34.1). Oxygen diffusion into the pores and through the product sulfate can limit the extent of sulfation obtainable. In fact, earlier work at Westinghouse indicated that calcium sulfides resulting from limestone sulfidation cannot be completely oxidized to $CaSO_4$ within a practical reaction time.[D4] Calcium sulfides prepared from dolomite sulfidation, however, were found to be more readily oxidized to $CaSO_4$. The inherent porosity in the dolomite's magnesium fraction is believed to be responsible for the more complete sulfation. The actual extent of sulfation depended on the dolomite's sulfidation level and the oxidation temperature. Conversion to sulfate was more complete at higher temperatures (800°C), but then there was risk of SO_2 release in the process.

Since efficient sulfur removal can be achieved with dolomites sulfided nearly 100%, the ability to oxidize completely sulfided dolomite is desirable. A set of experiments was conducted to determine the extent of oxidation achievable with sulfided dolomite as a function of the dolomite particle size and sulfidation extent.

TEST DESCRIPTION

We studied the oxidation of sulfided samples of Dolomite 1337 in thermogravimetric (TG) equipment. Sulfided samples were prepared in the TG apparatus, and the conversion of sulfide to sulfate was then tested

by having air flow over the samples at 500 to 900°C. The equipment used and the procedures followed are outlined below.

Dolomite 1337 from the Guelph formation, Niagaran group, Silurian system, was chosen for this test program because it typifies dolomites with good sulfur sorption reactivity. Dolomite 1337 is quarried by Pfizer Minerals, Gibsonburg, Ohio.

The data were obtained in a Du Pont 951 thermobalance system. A sized sample of dolomite was placed in a platinum wire mesh basket and suspended from the balance arm into a quartz reaction tube. The quartz tube was surrounded by a furnace that controlled the system temperature. A thermocouple positioned near the sample measured the reaction temperature. The reaction gas mixture, metered by linear mass flow controllers, continuously swept the sample. To allow operation in hot H_2S environments, we adapted (Figure D-1) a double-walled quartz tube configuration. An inert gas purged the bell jar region and passed through the slot for the balance beam in the aluminum housing. A baffle, which also prevented H_2S penetration into the balance mechanism, deflected the purge gas toward the outer tube section. The purge and reactant gases exited through the outer section of the reaction tube. The sample size (20 mg) and reaction flow rate (0.6 ℓ/min STP) were selected to minimize the effect of external mass transfer on the initial sulfidation rates.

The balance, controlled by a Du Pont 990 console, sends out a continuous electric signal that provides a reading of the weight of the sample as a function of time. The TG data are routinely stored on cassette tape using a FluiDyne analog-to-digital conversion system controlled by a custom-built system based on a Mostek microprocessor. Reduction of the data is carried out by rereading the data into a Wang calculator. Each weight datum is read to ± 5 μg, which corresponds to 0.03% sulfidation of a typical 10 mg sample of CaO. Data are stored on cassette tapes in the form of millivolt readings.

The testing procedure is as follows:

1. Size dolomite to the desired range.
2. Suspend a 20 mg sample in a platinum mesh basket from the balance arm.
3. Shock heat the sample (~ 800°C/min) by sliding the assembly into a preheated furnace (840°C with a 600 ml/min (STP) flow of N_2).
4. After complete calcination (~ 20 minutes), switch the gases to a sulfidation atmosphere (0.5% H_2S, balance N_2).
5. Monitor the sample weight as a function of time. Stop reaction at desired sulfidation level (e.g., 25%, 50%, 100%) by shutting off the H_2S flow.
6. Reduce temperature to desired level for oxidation.
7. Introduce air at 600 ml/min (STP).
8. Calculate oxidation extent from the weight gain and the initial weight of the dolomite and its calcium content.

The sulfidation and sulfation extents were calculated by assuming that only the following reactions occurred:

Sulfidation $\quad CaO + H_2S \rightarrow CaS + H_2O$

Sulfation $\quad CaS + 2O_2 \rightarrow CaSO_4$.

In reality, the magnesium fraction participates in the sulfur sorption. The compound $CaSO_4 \cdot 3\ MgSO_4$ was identified as a trace substance in one of the oxidized samples. In the higher temperature oxidations, the sulfide/sulfate reaction can occur, emitting SO_2.

TEST RESULTS

The extent of oxidation of the CaS obtained as a function of particle size and the extent of dolomite sulfidation is given in Table D-1. Samples were purged with oxygen until the rate of weight gain dropped below 0.01 mg/min (about 0.2% sulfating per minute). The sulfidation and oxidation reaction times for each sample are listed with the calculated percent sulfation in Tables D-1 and D-2. In these tables "% sulfated" means the percent of the sulfided material converted to sulfate by oxidation. The results indicate that fully sulfided dolomite

Table D-1

THE EFFECT OF PARTICLE SIZE AND SULFIDATION EXTENT OF THE CONVERSION OF CaS TO $CaSO_4$

	Sulfidation		Oxidation	
Particle Size, μm	% Sulfided	Time, min.	% Sulfated at 700°C	Time, min.
44-53	113	110	104 at 600°C	130
	105	100	70	250
	106	120	52	130
420-500	102	60	41	70
	50	10	43	110
710-840	113	120	39	100
	108	140	35	60
	46	10	54	180
	51	10	42 at 800°C	40
	25	5	63	12
1000-1190	109	140	42	100
	114	150	37	90
1410-1680	114	100	42	60

TABLE D-2

THE EFFECT OF TEMPERATURE ON CONVERSION OF CaS TO $CaSO_4$

	Sulfidation		Oxidation		
Particle Size, μm	% Sulfided	Time, min.	Temperature of Oxidation, °C	% Sulfated	Time, min.
710-840	100	145	500	4	80
710-840	100	145	600	13	90
710-840	100	145	700	20	130
710-840	100	145	800	68,34	140,160
710-840	100	145	900	58	40
710-840	50	10	800	14	50

cannot be completely oxidized at 700°C unless the particle size is smaller than 400 μm. Fine particles (50 μm), for example, can be completely sulfated.

The extent of oxidation possible improves with increased temperature (500-900°C), as indicated in Table D-2. The equilibrium SO_2 level, however, generated from the sulfide sulfate reaction, increases with temperature.

RECOMMENDATIONS

Additional TG tests should be performed to more clearly define the extent of sulfidation and the dolomite particle size for which complete sulfation can be achieved. When acceptable sizes and sulfidation extents are established, bench-scale, fluidized-bed tests should be conducted with off-gas analyses. These tests are needed to confirm the sulfate conversion and determine oxidation conditions that minimize SO_2 release.

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